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TECHNOLOGY UTILIZATION REPORT

Technology Utilization Division

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TUNGSTEN POWDER
METALLURGY

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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

TECHNOLOGY
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TUNGSTEN POWDER
METALLURGY

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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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FOREWORD

The Administrator of the National Aeronautics and Space Administration has established a technology utilization program for rapid dissemination of information on technological developments which appears to be useful for general industrial application. Tungsten metallurgy has received considerable attention in the aerospace industry because of its high strength at very high temperatures. This study on tungsten powder metallurgy was undertaken to explore the work done by NASA and others and to make this advanced state of the art more generally available.

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The Director, Technology Utilization Division
National Aeronautics and Space Administration

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INTRODUCTION

It is the purpose of this report to summarize recent developments in tungsten powder metallurgy technology as related to space vehicles and the less traditional applications. The customary use of tungsten as a carbide or as a minor alloying element is not considered here.

According to a 1910 paper by Fink, "Announcement has been recently made of the production of tungsten in a form in which it is ductile. This ductile tungsten would seem to be a new substance from the viewpoint of the physical chemist, . . . ".[1]* A contemporary account by Coolidge noted that "when work was first started on the problem of producing a ductile form of tungsten, the metal looked very uncompromising."[2] The succeeding technological developments over the following 40- to 50-year period have been detailed in a number of papers and books.[3-14] Reference (15) in 1959 marks the approximate beginning of production for space technology uses.

The importance of tungsten as an elevated temperature resistant material is suggested by the service temperatures of figures 1[16] and 2.[17]

Early advances in tungsten metallurgy were made in industrial laboratories with private funds. The greatest contributions to space-oriented tungsten technology have been made in Government funded laboratories or other facilities, of which the National Aeronautics and Space Administration is a notable example.

Tungsten as a Transition Metal

Solubility and melting temperature relationships with some corresponding Young's modulus values for *bcc* Group V to Group VIII metals and several neighboring elements are illustrated in figure 3.[18] From time to time, efforts have been made to arrive at a semi-theoretical correlation between melting point or some other physical property, such as heat of fusion and mechanical strength.[19, 20, 21, 22,] The exceptionally high melting temperature of tungsten makes such a correlation of more than ordinary interest. Table I, from a recent critical survey by Gschneider[23], indicates that the elastic modulus increases continuously in a horizontal direction from Group III to the first member of Group VIII, after which it decreases. The minimum melting points, however, tend to lie in Group VI (actually at Group V in the first series), and, therefore, the maximum melting temperature of tungsten does not coincide with the maximum ambient temperature modulus in the third transition series. At higher temperatures, the elastic strength of tungsten compares more favorably. For example, the modulus of tungsten at 1650° F is approximately the same as that of rhenium. The 20 000 000 psi advantage if iridium over tungsten at room temperature is reduced to 10 000 000 psi at 1650° F.[24] The same effect is shown in bulk modulus comparisons.[25]

The melting point-strength relationship is further illustrated for tungsten and other metals by an activation energy-melting temperature plot of the type advanced by J. E. Dorn. Figure 4[26] illustrates the generally good correlation obtained in such a plot, in which ΔH is an observed activation energy for creep, stress rupture, or self-diffusion. It has been shown that creep in metals is an activated process, and that, at high temperatures (above about 0.5

$F_2 + H_2$

$F_2 + B_2H_6$

$F_2 + N_2H_4$

$F_2O + C_8H_{18}$

$O_2 + Be$

9000

8000

7000

6000

5000

4000

3000

2000

Current classified solid propellants

NH_4ClO_4 + Al + Binder

RFNA + polyethylene

$N_2O_4 + N_2H_4$

$H_2O_2 + C_2H_5OH$

Black powder

TaC, HfC, melt

C, sublimes

ZrC, melts

W, melts

Hf B_2 melts

Ta B_2 melts

Fe, boils
Ta, melts

Ni, boils

Mo, melts
Cu, boils
Nb, melts

Ag, boils

Pb, boils

Fe, melts

FAHRENHEIT
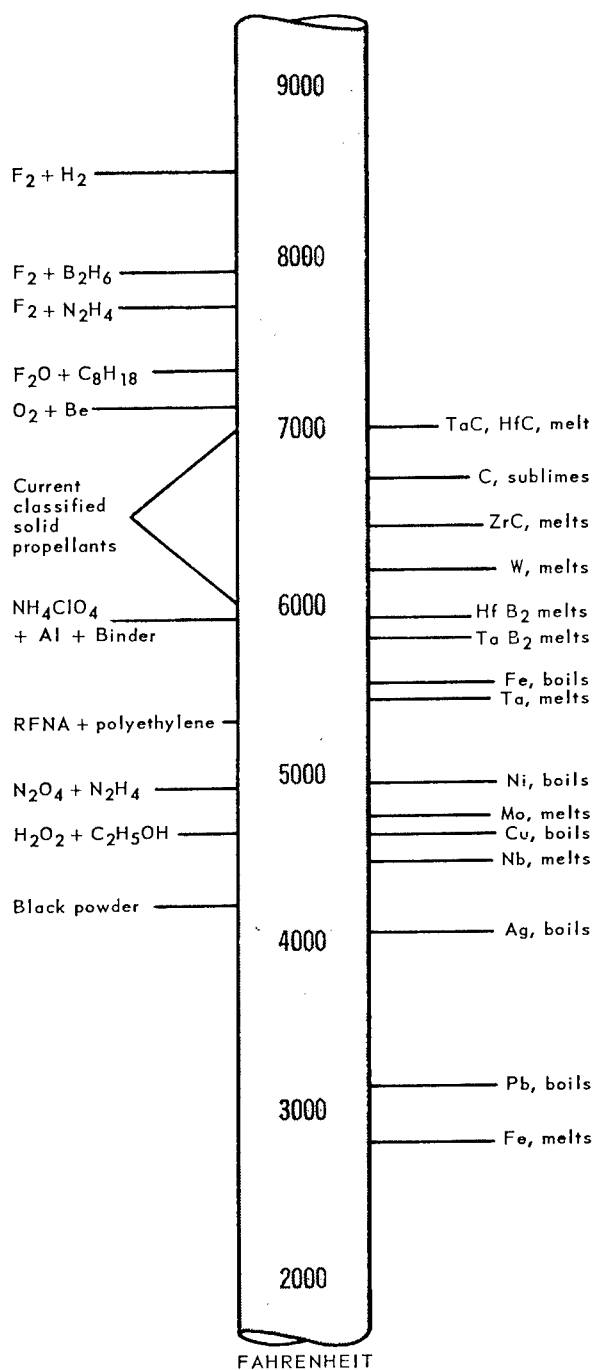
Figure 1.—Combustion temperatures of rocket propellants plotted against the melting and vaporizing temperatures of various component materials. [16]

TIME (HR)
100,000
10,000 ——— ONE YEAR
1000
100
10
1
0
0   1000   2000   3000   4000   5000   6000   7000
TEMPERATURE (°F)

REFRACTORY METALS

NUCLEAR ELECTRIC GENERATORS

ION ENGINE & THERMIONIC GENERATORS

HYPER-SONIC AIRCRAFT

NUCLEAR ROCKET

ROCKET NOZZLES

Figure 2.—High-temperature materials requirements. [17]

T_m), the activation energy for creep is usually the same as that for self-diffusion. The resistance of four refractory metal lattices to thermal disturbance is also reflected in the approximate threshold-of-recrystallization temperatures in

table II. [27] Such recrystallization is ordinarily associated with rapid loss in mechanical strength.

Finally, Conrad and Hayes [28] have arrived at a relation between the thermal component, τ^*, of the yield stress and the incremental fractions of the absolute melting temperatures for vanadium (V), chromium (Cr), iron (Fe), niobium (Nb), tantalum (Ta), and tungsten (W) (fig. 5). The fact that the thermal component can be correlated, as illustrated, suggests that the same dislocation mechanism may be rate-controlling in these metals. Futher, since the thermal component is independent of structure, it is concluded that the yeilding mechanism operates in overcoming the Peierls-Nabarro stress; i.e., the inherent resistance to strain of the bcc lattice.

The forging considerations illustrate the inherent strength advantage of tungsten at high temperatures. The fundamental reason for this characteristic strength in terms of electron configuration interaction has not been fully explained. There is little doubt however, that an optimum number of electrons in the unfilled 5d shell is involved. [29] For example, it has been suggested that the exceptionally high cohesive energy and elastic isotropy of tungsten have their origin in the powerful exchange spin interactions between the incompleted d-shells. [30, 31]

Some Considerations in Hardware Design

The foregoing summary has noted the inherent strength of tungsten metal. This is only one

2
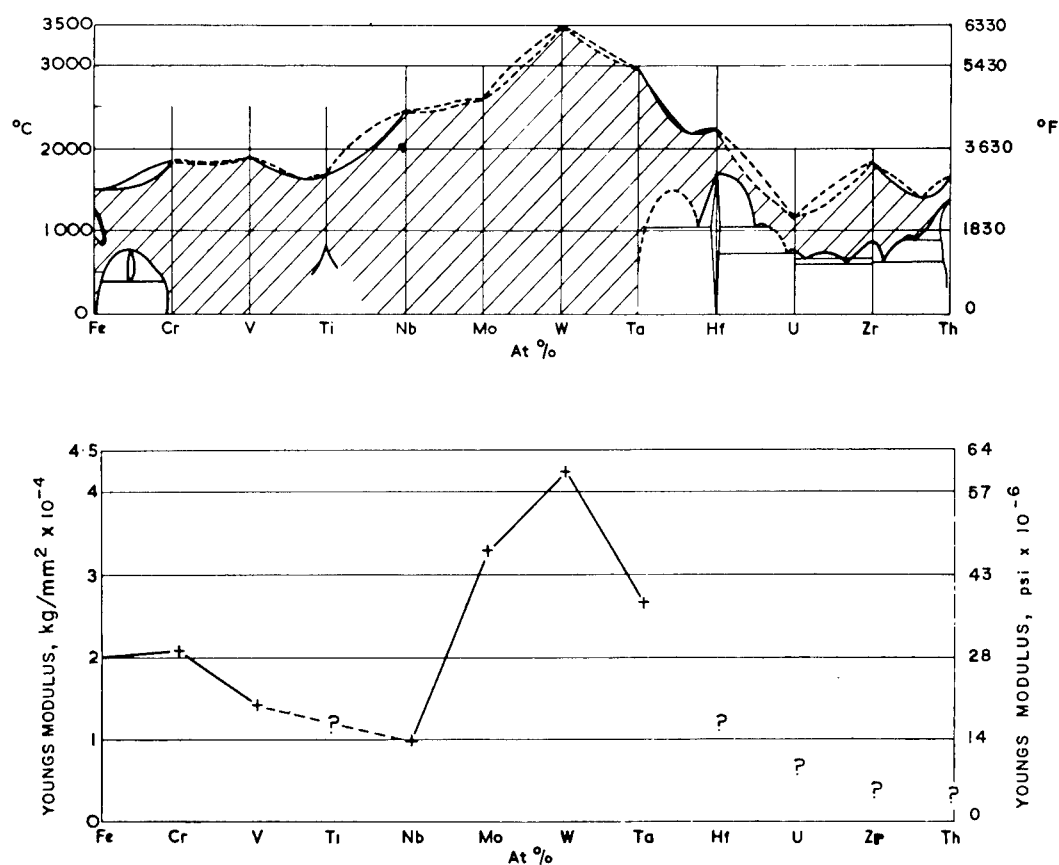
Figure 3.—Structural continuity in bcc metals (upper) and the corresponding Young's modulus (lower), illustrating the relative position of tungsten in the series. [18]

Table I.—Young's Modulus and Melting Point for Group III through Group VIII Transition Metals [23]

Group:	III	IV	V	VI	VII	VIII		
Element:	Sc	Ti	V	Cr	Mn	Fe	Co	Ni
Melting point, °F	2802	3034	3461	3407	2271	2798	2717	2647
Young's modulus, 10⁶ psi	11	15	19	35	29	30	30	28
Element:	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd
Melting point, °F	2735	3362	4474	4739	3938	4136	3560	2826
Young's modulus, 10⁶ psi	9.4	13	15	48	54	60	54	18
Element:	La	Hf	Ta	W	Re	Os	Ir	Pt
Melting point, °F	1688	4032	5428	6126	5720	5481	4429	3216
Young's modulus, 10⁶ psi	5.5	20	26	58	67	78	77	25

of several factors which may be important in a high temperature material. Following is a list slightly modified from Promisel:[17]

1. Operation to 4000° C (or higher temperature)
2. Strength-to-weight ratio
3. Creep strength
4. Stress-to-rupture strength
5. Fatigue
6. Thermal shock resistance
7. Ductile-to-brittle temperature transition

3

Table II.—Approximate Temperature of Recrystallization Onset for Increasing Deformation of Niobium, Tantalum, Molybdenum, and Tungsten [27]

Material	Purity	Mode of deformation	Begining of recrystallization, after % deformation at °C			
			10%	30%	60%	90%
Nb	99% Nb_____ 0.11% O 0.0027% H 0.06% C	Cold rolled_____	1200	1100	1025	1020
Ta	99.8% Ta_____	Cold rolled, cold pressed (hydrostatic pressure)__	1280	1250	1250	1200
Mo	0.1–0.2% C_____ Some 1/10% Fe Traces of Si ~0.002% O	_____	1200	1070	980	_____
W	99.6% W_____ Commercially	Hammered, with process annealing (below recrystallization temperature).	1560	1500	1430	1420
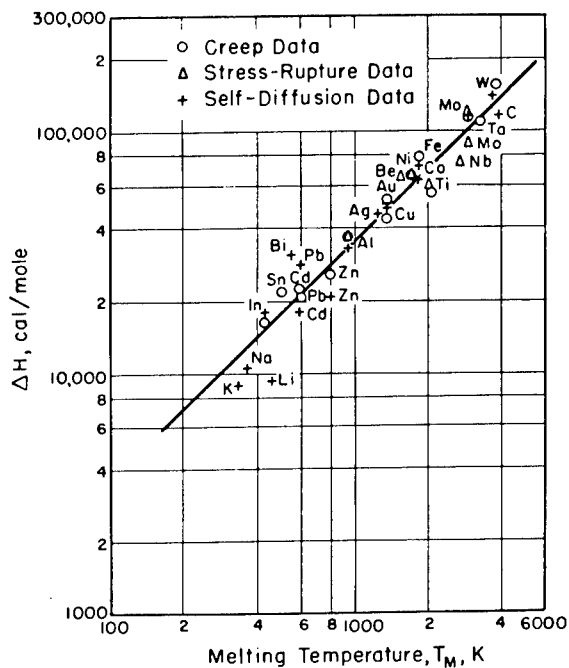
Figure 4.—Correlation of the activation energies for creep, stress-rupture, and self-diffusion with the melting temperature. [26]

Figure 5.—Correlation of thermal component of the yield (stress τ^* with the parameter $(T-T_o)/T_m$ for the bcc metals. [28]

8. Fabricability and joinability
9. Oxidation resistance
10. Thermal, electronic, and nuclear properties
11. Resistance to molten metals

12. Impact resistance
13. Erosion resistance
14. Availability-sheet, bar, forgings, tubing, extrusions.

In design work, more or less weight is given to one item or another in the foregoing list, depending on the details of application. Com-

monly this takes the form of a "trade off" in which a less critical requirement is sacrificed in favor of a fully necessary property.

Tungsten is outstanding in general with respect to items 1, 3, 4, 11, and 13. Item 9, oxidation resistance, is perhaps the greatest problem associated with this metal and its alloys. Strength-to-weight considerations commonly restrict tungsten to operating environments above 3000° F. Tungsten is notably less favorable in comparison to many lower melting metals with respect to items 7 and 8. It is difficult to generalize much further in view of the differences in details of applications requirements.

Mineral Reserves

Estimates of U.S. reserves of tungsten have been reported by McKelvey[32] and by Nelson.[33] These amount to approximately 70 000 to 80 000 tons as metal. This tonnage appears adequate for the present, but the long range outlook is questionable. Tungsten is currently imported for the major portion of U.S. requirements because of the lower price of foreign concentrates.

POWDER PRODUCTION

Reduction to Metal

Because of the high melting point of tungsten, its production is dominated by powder metallurgy processes rather than by fusion associated techniques. The common raw materials, wolframite and scheelite, may be treated as follows:

$$4FeWO_4 + O_2 + 4Na_2CO_3 = 4Na_2WO_4 + 2Fe_2O_3 + 4CO_2$$

$$CaWO_4 + 2HCl = H_2WO_4 + CaCl_2$$
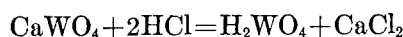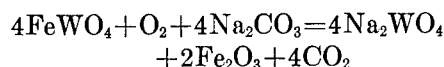
The subsequent purification steps are designed to yield as pure a furnace feed as is consitent with economic considerations. The purified product is ordinarily the ammonium paratungstate: $5(WH_4)_2O \cdot 12WO_3 \cdot xH_2O$ or tungstic acid:

$$5(NH_4)_2O \cdot 12WO_3 \cdot 5H_2O + 10HCl + 2H_2O = 10NH_4Cl + 12H_2WO_4$$
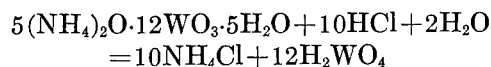
The paratungstate is ordinarily fired in air to form yellow WO_3. It is also possible to hydrogen-reduce from the paratungstate.

The oxide is reduced to WO_2, by degrees, in a flowing hydrogen atmosphere. The equilibrium, under furnace conditions, of the reaction

$$WO_2 + 2H_2 = W + 2H_2O$$
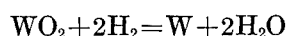
is very favorable to the production of tungsten metal. Griffis[34] obtained experimental equilibrium data for the above reaction. These data are averaged in table III.
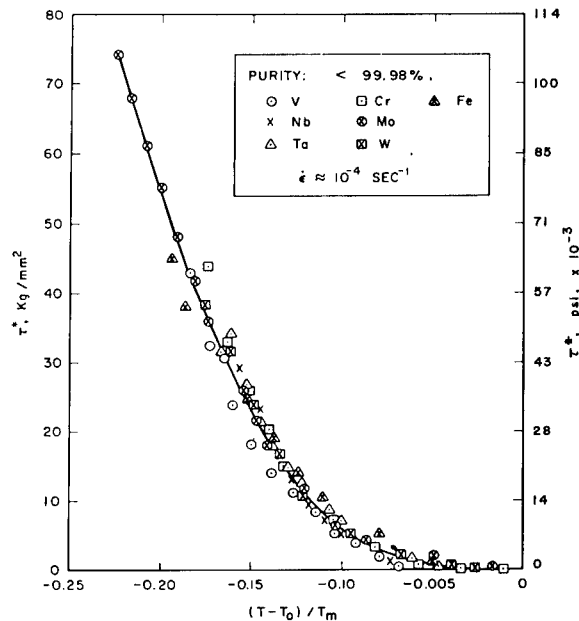
The favorable circumstances for reduction are illustrated by the comparatively large equilibrium P_{H_2O}/P_{H_2} values. Figure 6 from Chang[35] is based on thermodynamic calculations and compares the equilibria for the general reaction:

$$M_mO_{n(s)} + nH_{2(g)} = mM_{(s)} + nH_2O_{(g)}$$
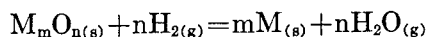
For WO_2 and other oxides, the areas below each of the curves are those in which metal production is favored. For either the production of metal powder from the oxide or sintering of tungsten in hydrogen, it is apparent that substantial amounts of water vapor can be tolerated at even fairly low temperatures. However, in the production of powder, water vapor is ordinarily maintained at a low level to keep the reduced product as free of oxide as possible. The production of tungsten metal powder by

Table III.—Equilibrium Data for the System WO_2-H_2-W-H_2O

Temperature, °C	$K_p = P_{H_2}O/P_{H_2}$ [a]
500	0. 12
600	0. 21
700	0. 35
800	0. 48
900	0. 68
1000	0. 94

[a] Averaged from Griffis' data.

5
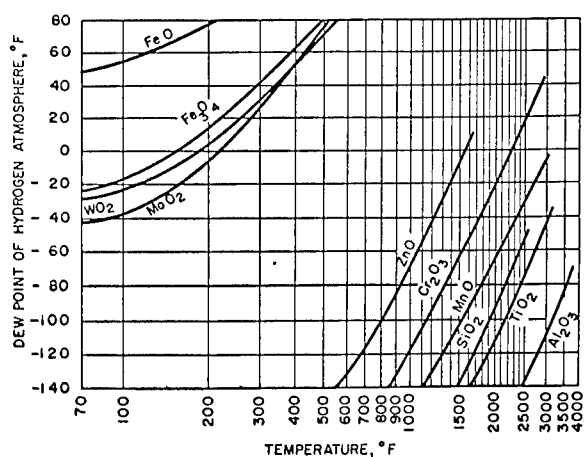
Figure 6.—Metal-metal oxide equilibria in hydrogen atmospheres. [35]

the passage of WO_3 in boats through a hydrogen tube furnace is affected by several factors:

Reduction temperature

Rate at which temperature is increased

Rate of hydrogen flow

Total load and depth of load in each boat

Rate of boat passage through the tube furnace.

Most tungsten powder is produced in the size range from about 1 to 10 microns. Very fine powders require equally fine oxide starting material, a rapid flow of hydrogen through the furnace, a low reduction temperature, and a minimum time in the furnace consistent with complete reduction. Coarse powders are produced by higher reduction temperatures and longer furnace dwell times at temperature.

The foregoing outline is intended only to furnish a perspective view of tungsten powder production. For further details, references cited in the preceding section should be reviewed.

Recently, hexamine has been used as an auxiliary reducing agent for WO_3.[36,37] The type of reduction involved is illustrated by the following expression:

$$(CH_2)_6N_4 + 6WO_3 = 6W + 6CO_2 + 6H_2O + N_2$$
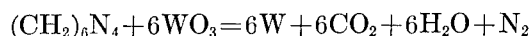
The use of hexamine is said to permit the rapid production of high purity tungsten with particle size distributions which may be predetermined and reproduced over a wide range.

Details of two Soviet rotary furnaces for producing tungsten powder have appeared.[38] The hydrogen reduction of WO_3 in these furnaces is reported to yield a more uniform product than that produced in a four-tube muffle furnace which is also described. Further, the rotary furnaces are more amenable to automation. Three-stage reduction of WO_3 in the manufacture of thoriated tungsten produced high quality wire in Czech research.[39] A number of studies dealing with WO_3 reduction have been reported by Philips Research Laboratories workers. The retarding action of water vapor during the hydrogen reduction of WO_3 is less pronounced with doped products. Potassium silicate and $K_4SiW_{12}O_{40}$ increase the reduction rate of WO_3 in deep layers.[40] The influence of doping agents on the growth of tungsten crystals during hydrogen reduction of the oxide has been studied. The action of potassium silicate in the growth of large crystals is related to the formation of α-tungsten relatively early in the reduction process.[41] Alumina, on the other hand, opposes growth of primary tungsten crystals. Grain sizes and shapes of pure, thoriated, and silicate doped tungsten powders have been studied by means of an electron microscope.[42]

Powder, Size and Purity

In the last 10 years, there has been a distinct trend toward the production of higher purity tungsten powder intended for the fabrication of shapes to be severely worked. At the same time, it should be noted that powder purity is only one factor in the successful production of mechanically worked parts, that is, acceptable powder chemistry will not guarantee freedom from failure during deformation of a shape made from the powder. The metallurgical structure of a wrought preform of powder metallurgy origin may determine the success or failure of a forming operation. Because some impurity levels in starting powders may be altered during subsequent consolidation and shaping, and because factors such as grain size are important, it is difficult to specify critical impurity limits. "Substantial" impurity contents ordinarily are damaging. Table IV[43] illustrates the starting powder composition differences between two materials exhibiting satisfactory forging response (Vendors A and B) and two materials with which severe cracking was experienced during efforts to forge them (Vendors C and D). Cracking

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Table IV.—Chemical Analyses of Tungsten Forging Billets [a][43]

Element, ppm	Unalloyed sintered W (powder metallurgy)			
	Vendor A	Vendor B	Vendor C	Vendor D
C	<10	60	30–50	60
O	<15	21	63	40
N	<5	4	4	10
H	<5	<3	3	-------
Al	<10	21	-------	-------
Ca	10	<5	-------	10
Si	<10	3	10–100	50
Fe	<10	5	1000	20
Cr	<10	4	-------	<10
Ni	<10	7	-------	30
Cu	<10	<1	-------	-------
Mn	<10	-------	-------	10
Mg	<10	<3	-------	<10
Sn	<10	-------	-------	-------
Cb	-------	-------	-------	<10
Ti	-------	-------	-------	<10
As	-------	<3	-------	-------
K	-------	<30	-------	-------
S	-------	<30	40	-------
Mo	<30	30	30–50	100
P	-------	-------	50	-------
Co	-------	-------	-------	-------
V	-------	-------	-------	-------
Pa	-------	-------	-------	-------
Th	-------	-------	-------	-------

[a] Analyses were supplied by sources.

was expected in the latter, considering the high levels of some impurities. Table V[44] illustrates the variety of impurity level specifications as of about 1960. These specifications may be compared to Materials Advisory Board recommendation for maximum allowable impurities in tungsten sheet (table VI[45]) and those contained in an AMD Specification (table VII[46]). Carbon, oxygen, hydrogen, and nitrogen, if not present in too great amounts, may be reduced to acceptable levels during sintering; nonvolatile impurities will remain in the sintered product. Producers of powder intended for the production of tungsten to be mechanically worked to hardware shapes generally like to keep Fe, Si, Al, Mo, and Ni at low levels. The effects of powder quality on subsequent properties of tungsten have been summarized by Allen. [47]

An extensive powder evaluation program was carried out as part of a Navy contract to develop large (48 in. × 18 in.) tungsten sheet production techniques by powder metallurgy as contrasted with an arc-melting approach. Table VIII[48, 49] illustrates the variety of powders investigated. The undoped powder produced by single-stage hydrogen reduction of ammonium paratungstate, ranging in particle size from 1 to 20 microns, and having the analysis shown in table IX, was selected for the full-scale pilot phase of this work.

The powder particle size distribution appeared to be the major factor involved in the prediction of powder behavior through consolidation and subsequent working. Fine powders generally sintered the highest densities, but were also the most difficult to press and to work in the sintered condition. The coarse, heavy density powders pressed well and provided high green strength, but were difficult to sinter up to the desired levels. The use of blended combination of fine and coarse powders provided types with excellent consolidation and working properties, but the size distribution tended to be carried through into the sintered and wrought product, resulting in a nonheterogeneous structure difficult to work.

The undoped powder produced by single stage reduction of paratungstate appeared to provide a material which would best suit the production facilities and proposed material application at the start of the program (table X). At the end of the program, it was suggested that oxygen content be held to 300 ppm maximum, and that the combined carbon and nitrogen should not amount to more than 20 ppm. Further, if possible, residual impurities other than interstitials should be held to below 20 ppm.

The problem of developing a rigid specification for tungsten powder to produce a satisfactory product in different consolidation facilities should be noted. For example, the 3.7–4.0 optimum particle size range of table X might possibly be increased to 4.0–4.3 and still produce suitable end product, with the availability of higher sintering temperatures. [48]

Ultrafine Powders

The interest in ultrafine metal powders is illustrated by extensive NASA work. [50] In

Table V.—Typical Purity Specifications for Tungsten Powder as of 1960 [44]

	Impurity content, wt%, [a]										
	O	N	H	C	Al	Ca	Fe	Mo	Ni	Si	W
Producers:	*For use in powder metallurgy product*										
Cleveland Tungsten	0.20	-----	-----	0.01	-------	-----	0.01	0.005 0.030	--------	0.01	------
Fansteel	0.10	0.005	0.005	0.02	0.005	-----	0.02	0.02	0.02	--------	------
Firth Sterling	0.30	-----	-----	0.01	0.01	0.01	0.02	0.01	0.02	0.01	------
General Electric (Lamp Metals and Components Department)	0.01	-----	-----	0.003	<0.001	-----	0.002	0.003	<0.001	<0.001	------
Reduction and Refining	0.05	-----	-----	0.001	0.002	-----	0.001	0.05	0.002	0.003	------
Sylvania	0.15	-----	-----	-----	-------	-----	0.002	--------	0.001	--------	------
Wah Chang	0.030	-----	-----	0.002	<0.002	-----	0.003	0.0500	<0.001	<0.003	------
Westinghouse	-----	-----	-----	-----	0.005	-----	0.005	0.002	0.002	0.01	------
Consumers:											
Aerojet General (Sacramento)	0.02	0.02	0.01	0.025	--------	-----	0.05	0.015	--------	0.05	------
Allison Division of General Motors	0.5	0.03	-----	0.001	<0.001	-----	<0.001	<0.003	<0.001	<0.001	------
General Electric Research Lab	0.01	0.001	-----	0.005	<0.001	-----	<0.001	0.003	<0.001	<0.001	------
Raytheon	-----	-----	-----	-----	0.01	-----	0.03	0.01	0.03	0.01	------
Universal Cyclops	0.015	0.003	-----	0.005	--------	-----	0.0005	0.0025	0.0004	0.0003	------
	For use in melted product										
General Electric Research Lab	0.01	0.001	-----	0.005	<0.001	-----	<0.001	0.003	<0.001	<0.001	------
Oregon Metallurgical Corp	0.03	-----	-----	0.01	--------	-----	--------	--------	--------	--------	99.9 min.
Universal Cyclops	0.01	0.003	-----	0.005	0.001	-----	0.003	0.001	0.001	0.002	------
Wah Chang Corp	0.010	-----	-----	0.002 0.010	<0.002	-----	0.003	0.05	<0.001	<0.003	------
Westinghouse (Blairsville)	-----	-----	-----	-----	0.002	-----	0.002	0.01	0.002	0.002	------

(a) 0.0001%=1 ppm.

the case tungsten, there have been several incentives for fine powder production. Among these are the development of dispersoid strengthened alloys, the consequent decrease in diffusion distance where solid solution alloys are being made from elemental powders, and reduction sintering temperature. Figure 7 illustrates the high as-sintered density and small, uniform grain size achieved by the low temperature sintering of ultrafine tungsten powder. It has been demonstrated in Los Alamos work[51] that additions of up to 25 percent of ultrafine

tungsten (surface area: 3.7 m²/g) to conventional powder can increase as-sintered densities up to about 9 percent greater than densities obtainable using conventional powder.

Lamprey and Ripley have made ultrafine tungsten powder by hydrogen reduction of WCl_6.[52,53,54] The powder so produced had a diameter of about 0.02 to 0.03 micron. Green compacts of this powder were sintered to 94 percent theoretical density at the comparatively short time and low temperature of 30 minutes at 1550° C, that is, at about 1000° C lower
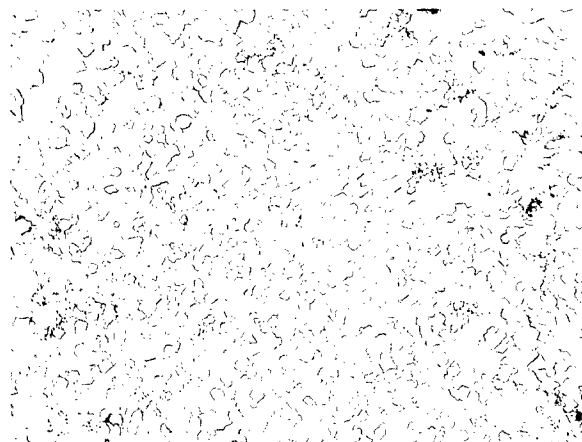
Figure 7.—As-sintered tungsten, ultrafine powder (0.015–0.050 micron) pressed at 5000 psi and sintered at 2280° F (1250° C) in hydrogen for 15 hours (Battelle).

Table VI.—Materials Advisory Board Recommended Sheet Composition [45]: Maximum Allowable Chemicals

Element	ppm, max	Element	ppm, max
C	50	Cu	20
O	50	Sn	20
N	20	Ca	20
H	10	Co	10
Mo	100	Pb	10
Fe	50	Mg	10
Si	40	Mn	10
Al	40	Ag	10
Zr	50	V	10
Cr	20	Ti	10
Ni	20		

W 99.95% minimum, by difference

Table VII.—Impurity Limits, SAE Specification AMD 78 BU, for Tungsten Forgings—Pressed, Sintered, and Forged, 1–15–63 [46]

	%
W	99.950 min
Mo	0.010 max
C	0.006 max
O	0.006 (60 ppm) max
Al	0.002 max
Fe	0.002 max
Cu	0.002 max
Ni	0.002 max
Si	0.002 max
N	0.002 (20 ppm) max
H	0.001 (10 ppm) max
Others, each	0.001 max

Table VIII.—Characteristics of Powder Lots and Blends Evaluated [48,49]

Code No.	Type	Average particle size, microns	Density, g/in.^{3}
1	Undoped	1.18	34.5
2	Undoped	7.10	70.4
3	Alkali-silicate doped	6.00	47.8
4	Alkali-silicate-carbon doped	5.80	52.9
5	Alkali-silicate doped	5.60	54.2
6	Alkali-silicate doped	4.80	51.0
7	Alkali-silicate-aluminum doped	4.30	52.2
8	Undoped	4.30	49.8
9	Undoped	6.10	90.8
10	Undoped	3.90	59.5
11	Undoped	3.60	56.4
12	Alkali-thoria doped	4.80	60.4
13	Undoped blend	2.60	61.2
14	Undoped and doped blend	2.00	43.8
15	Undoped blend	2.50	54.6
18	Undoped	5.00	79.3
19	Undoped	1.15	45.2
20	Undoped	3.65	67.7

than is required for ordinary tungsten powder in this length of time.

Ultrafine tungsten powder currently offered for sale by one producer is advertised to have the following properties:

Surface area___ 10 to 20 meters^2-g
Particle size___ 0.015 to 0.030 micron
Particle shape_ Spherical
Particle size distribution. Practically no size variation.
Bulk density___ Less than 1 g/cm^3
Stability in air_ Reactive (possibly pyrophoric)
Stability in water. No apparent reaction
Fluidity_____ Very fluid.
H$_2$_____ 0.001%
N$_2$_____ 0.001%
O$_2$_____ 1.0% max.
W_____ Nominal balance

As described in unpublished work at Battelle Memorial Institute, powder ranging in average particle size between 0.1 and 0.4 micron has been made by hydrogen reduction of suspended submicron particles of WO$_3$. Tung-

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Table IX.—Chemical Analysis of Tungsten [48,49] Powder Selected for Full-Scale Pilot Phase

Impurity element	Content, wt %	Impurity element	Content, wt %
O	0. 026	Fe	0. 001 —
N	0. 0005	Mg	0. 001 —
C	0. 001	Mn	0. 001 —
Ag	0. 001	Mo	0. 010
Al	0. 001 —	Ni	0. 001 —
Ca	0. 001 —	Si	0. 005 —
Cu	0. 001		

Table X.—Suggested Tungsten Powder Requirements for Tungsten Sheet Production [48]

Fisher average particle size	3.7–4.0 microns
Particle size range	1–20 microns
Scott density	60–70 g/in.^{3}
Maximum impurity levels:	
O_2	800 ppm
N_2	50 ppm
C	50 ppm
Mo	100 ppm
Fe	50 ppm
Si	50 ppm
Other metallics	10 ppm

Table XI.—Submicron Tungsten Metal

Typical analysis:

	%		%
C	0. 07	Mn	0. 001
Al	0. 002	Na	0. 001
Cr	0. 001	Mg	0. 001
Be	0. 002	K	0. 001
Fe	0. 01	Cu	0. 001
Mo	0. 005	W+O	99. 88
Si	0. 02	O	1.

Typical physical properties:
Color	Black
Crystal form	W
Particle shape	Crystalline
Particle size	<0.01−0.07, avg 0.011 micron.
Surface area	29 sq m/g
Bulk density	35 lb/cu ft
Stability	Pyrophoric in air

sten oxide, aerosolized in a hydrogen stream, was carried into a horizontal reaction chamber at 1450° F. There was little settling out of the reduced product in the suspending hydrogen stream at linear travel rates of 3 to 11 feet per minute.

Submicron tungsten powder has also been made by arc vaporization of WO_3 followed by reduction by hydrogen of the very fine oxide produced.[55] BET surface measurements gave a value of 29 meters^2/gram or 0.011 micron on a spherical diameter basis. In this work, it was observed that tungsten particles having surface areas greater than 20 meters^2/gram were pyrophoric when exposed to air. Table XI[56] characterizes the tungsten produced by this method in pilot scale runs. Low temperature oxide reductions, for example, 600° C for a 24-hour period, yielded powders with high surface areas (about 30 meters^2/gram), but also with high oxygen content. Correspondingly reductions at 800° to 850° C produced powders with lower residual oxygen, but also

lower surface area (5 to 10 meters^2/gram). At the beginning of the work described above, a state-of-the-art survey for submicron powders was made.[57]

An Air Force program to develop defect free, high formability tungsten flat rolled sheets using ultrafine tungsten powder (0.08 to 0.2 micron), inert working atmosphere, and high fabrication temperatures is in progress.[58] A summarizing, final report for this program has not been received.

Discussions of subsieve particle size analyses of tungsten have recently appeared.[59, 60]

Spherical Powders

Spherical tungsten metal powders have become important with the development of evaporation-cooled rocket nozzle throat sections and porous tungsten ionizers for rocket engines. NASA has sponsored a substantial amount of the research and development in these and bordering areas, as well as having carried out much research in its own laboratories.

Several procedures have been followed in making small tungsten spheres. One process uses a fluidized bed reactor in which seed particles in the 1- to 10-micron size range constitute nuclei for the growth of spherical powder by the accretion of tungsten from hydrogen reduced WF_6.[61] Tungsten granules in the 200- to 400-micron size range, containing a few percent by volume of seed, are now

available commercially. This material has been consolidated by gas pressure bonding into special shapes or into sheet bar material.

Spherical tungsten can also be made by the use of a plasma torch.[62, 63] Tungsten powder can be spheroidized, in principle at least, by dropping it through a resistance-heated graphite tube.[64] One producer has made spheres in the range 75 to 150 microns diameter, starting with 1/16-inch diameter tungsten wire.[65] Presumably, an arc process of one kind or another is used.

The use of the plasma arc for producing tungsten spheres has been described in detail in a British publication.[66]

The sizing and application of spherical tungsten powders has been reviewed in detail in an AIME publication.[67]

Electrolytic Powder

Pure tungsten can be deposited from an aqueous solution only with difficulty if at all. Ordinarily, only an alloy of one kind or another can be formed. Greater success has been possible by the deposition of tungsten from molten salt baths. Using either a WO_3 or a scheelite feed, and an $Na_4P_2O_7$-$NaCl$-$Na_2B_4O_7$ electrolyte, coarse dendritic powders of tungsten have been deposited.[68] The product had higher flow rates and better compressibility than hydrogen-reduced tungsten powder.[69] However, the large particle size peculiar to the electrowinning process effectively prevented conventional sintering to a high-density material. Densities 92 percent of theoretical were obtained by hot swaging the presintered tungsten in stainless steel sheaths.

CONSOLIDATION

Since tungsten metallurgy begins with the metal in powder form, powder consolidation is of interest whether or not the final product passes through a fusion stage. Although the most important metal powder consolidation procedure consists of compaction to shape in a die followed by solid state sintering, there is a variety of modifications of this general procedure. Only those of either current or potential interest in the consolidation of tungsten are noted in the following sections.

Cold Mechanical Compaction—Some General Considerations

The only important tungsten powder compacting method for the production of green ingots for manufacture of rod, wire, and narrow strip is solid die pressing. The compacts customarily range in size up to 2 feet in length, 1 inch in thickness, and 2 inches in width, and are made by simple lateral pressure in a rectangular steel die. These are presintered at 1100° to 1300° C, followed by self-resistance sintering to about 90 percent of theoretical density, and then worked to shape by various mechanical means. In the newer applications for consolidated tungsten, large pressings and more complicated shapes have been required. Some of these must be able to withstand machining in the green condition. The con-

sequent demand on the mechanical pressing stage of consolidation has encouraged the continued study of tungsten powder compactions. There is no fully acceptable expression to describe accurately the extent of densification versus applied pressure for tungsten, as well as other powders, although many have been suggested. Heckel[70] found the relation between as-pressed density and applied pressure to be expressed by the equation:

$$\ln\left(\frac{1}{1-D}\right)=KP+A$$

where:

    D is the relative density (that is, the ratio of the density of the compact to full density)

    P is the applied pressure

    K is a proportionality constant related to the yield strength of the metal

    A is a constant.

For tungsten, Heckel found $K=7.6\times10^{-6}$ psi^{-1} and $A=0.62$. Heckel's and other densification expressions have been critically reviewed by Donachie and Burr[71], who conclude that the previously noted equation allows at least an educated first guess at pressure-density values. Values of percent porosity as a function of pressure have been reported for several sizes of samples, by Shapiro.[72] The mean particle

Table XII.—Compression of Tungsten Powder[72]

Pressure, kg/cm²	% Porosity			
	Mixed size	"A"	"B"	"C"
Zero	60. 3	58. 1	56. 6	56. 3
616	47. 9	48. 5	48. 6	48. 1
921	45. 7	46. 2	46. 4	46. 2
1246	43. 8	44. 3	44. 5	44. 4
1578	42. 0	42. 5	42. 6	42. 8
1904	40. 6	41. 1	41. 1	41. 2
2208	39. 0	39. 7	39. 7	39. 9
2852	36. 4	37. 1	37. 1	37. 3
3475	34. 0	34. 4	34. 6	35. 1
4125	31. 7	32. 3	32. 5	32. 9
4843	29. 7	30. 1	30. 3	30. 9
5480	27. 7	28. 3	28. 2	29. 0
6137	26. 1	26. 5	26. 5	27. 2
6761	24. 4	24. 9	25. 0	25. 9

diameters of samples "A," "B," and "C" of table XII were 39, 45, and 58 microns, respectively. Data for sample "C" are plotted in figure 8, along with data for some other powders to illustrate the comparative resistance of tungsten to compaction forces. The curve for tungsten is in good agreement with data for isostatic compression of medium size tungsten particles reported in reference (73), but the density is greater than that also reported in reference (73) for fine particles, as is to be expected from powder metallurgy experience with the finer tungsten powder sizes.

Factors affecting the compaction of tungsten powders have been investigated and summarized by Poster,[74] who reached the following general conclusions:

(1) The formation of green compacts from tungsten powders depends to a large extent upon mechanical interlocking of the particles, since there is little deformation under pressure. Interlocking depends upon the use of irregular-shaped particles.

(2) Irregular-shaped tungsten particles, which can be produced by the standard method of hydrogen reduction of tungstic oxides, produce stronger but less dense green compacts than do regular-shaped particles made by the same process. It has been found that the strength of com-

pacts made from these irregular particles continues to increase for pressures beyond that which produces maximum density. Density and strength values approach maximum values at about the same pressure for compacts made from the more regular-shaped powder particles.

(3) It has also been shown that irregular-shaped electrolytic powder particles produce stronger compacts than hydrogen-reduced powder of the same particle size.

(4) Finer tungsten powders produce less dense green compacts than do coarser powders. The reason for this is the increased friction during pressure application for the fine powders.

(5) Particle-size distribution plays a major role in the formation of dense tungsten compacts. The maximum packing density obtained with two powders which measure 25 and 1.5 microns is at a ratio of approximately 80 percent of the coarser and 20 percent of the finer powder.

Isostatic Compaction

Isostatic compaction of tungsten powders has been a very successful way of circumventing the problems of obtaining uniform densities in large compacts by solid die pressing.[73, 75] Isostatic compaction dates back at least as far as 1913, when tungsten slugs were compacted by Madden (H. D. Madden, U.S. Pat. 1 081 618 Dec. 16, 1913, to Westinghouse Lamp Corporation). A 1954 paper describes the hydraulic pressing of tungsten tubing by a radial compacting process.[76] The isostatic process is in general use for the production of large tungsten slabs and billets where sintered densities must ordinarily reach minimums of about 90 to 92 percent if mechanical working is to be effected without failure by fracturing. The term "isostatic pressing" refers to any compacting operation in which pressure is applied equally in all directions through an appropriate transmitting medium. The medium may be water, oil, a gel, rubber, suitable powders, gases, and such. Hydrostatic pressing refers to the use of a fluid for transmitting the pressure, and gas pressure bonding refers to particular situations where gases are employed at elevated temperatures. In some instances, the process may be only partially isostatic, for example, when
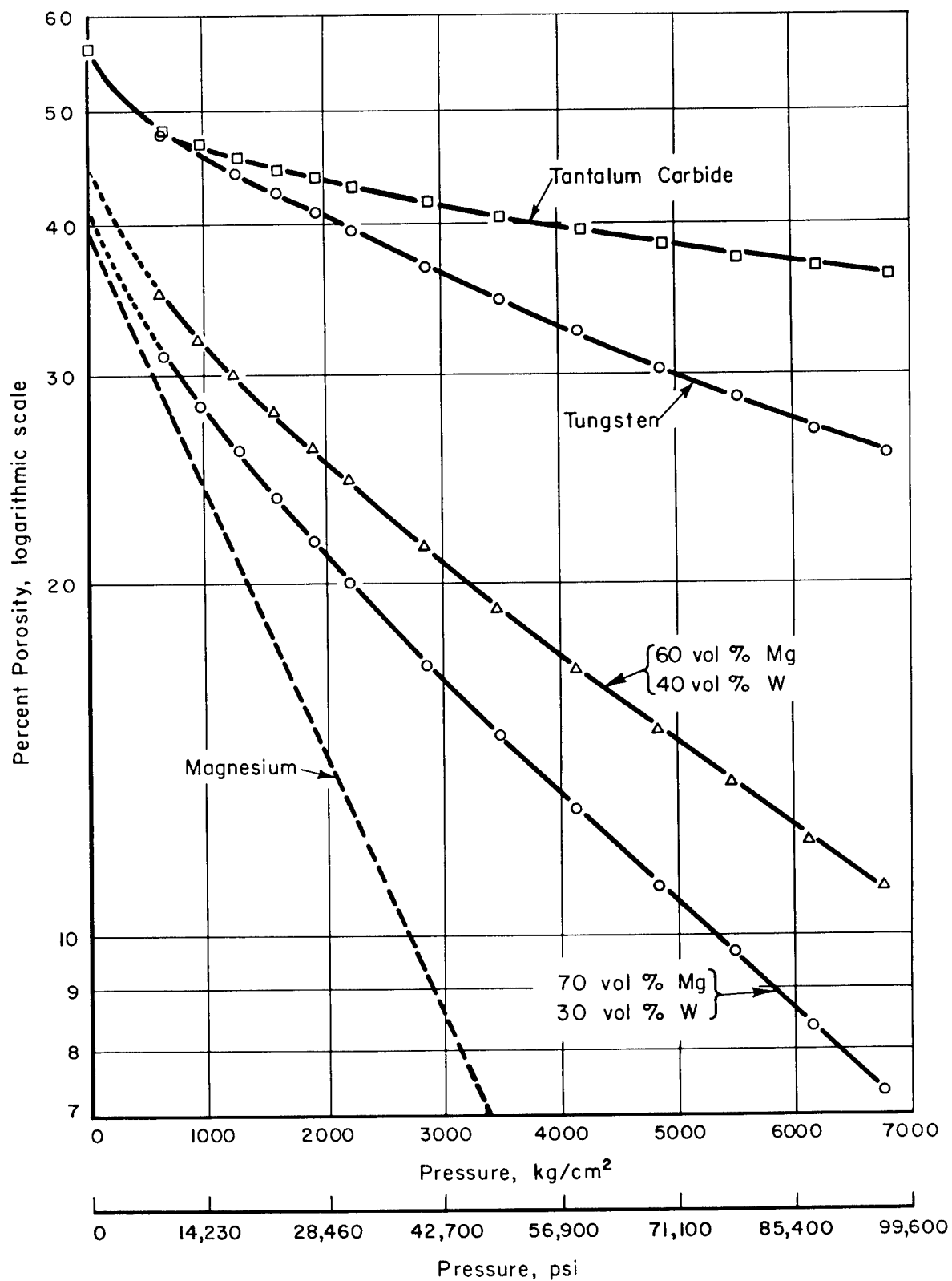
Figure 8.—Compressibility of tungsten powder compared to various other powders. [72]

only equal radial pressures are applied. The use of an isostatic pressing procedure avoids the disadvantages which arise from the influence of solid die walls during die pressing and which result in nonuniform density in either a large powder mass, unfavorable shape, or unfavorable dimensions. Commonly, metal powder is loaded into a rubber or plastic container. The container is partially evacuated, after which hydraulic pressures are applied to the external surfaces of the container. The as-cold compacted product ordinarly will withstand reasonable handling, without crumbling. This general procedure is especially useful in consolidating tungsten powders where density inhomogeneities have a more than ordinary effect on the subsequent workability of the as-sintered shape.

An interesting recent modificaton of the fluid isostatic technique involves the substitution of a preformed gel, elastomer, or other flexible mold material as the pressure-transmitting medium, This allows the isostatic pressing of tungsten shapes.[77] The improvement in density with increasing increments of pressure for pliable mold compaction of tungsten as compared to conventional solid die compaction has been demonstrated in Frankford Arsenal work.[78] At a compacting pressure of 60 000 psi, there was a 13-percent improvement in density of a simple cylindrical tungsten shape when the pliable mold was used (fig. 9). A NASA technical brief[79] suggests the use of barrel shaped chambers in rubber molds for the isostatic pressing of tungsten cylinders. For molding tungsten microspheres, pressures up to 56 000 psi were applied. Decrease in ram pressure was accompanied by deflection of the mold wall away from rather than toward the compact. This avoided fracture of the weakly bonded compact during unloading.

In the work on the compaction of tungsten powder for sheet production, previously referred to [48], it was concluded that isostatic pressing in the range 30 000 to 35 000 psi should be satisfactory for preparation of green compacts. Pressing at 20 000 psi tended to result in low sintered densities. There did not appear to be any adverse effect, but also there was no advantage in the subsequently sintered sheet bar, from compacting pressures as high as 50 000 psi.

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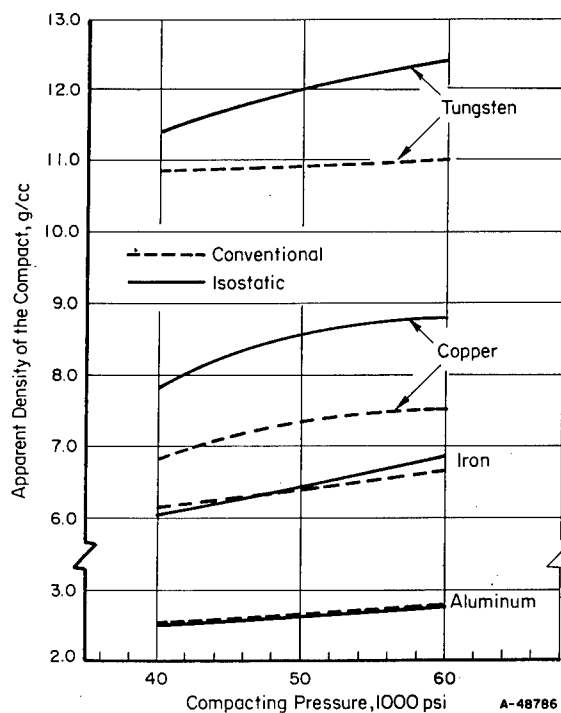
Figure 9.—Comparison of the compressibilities of several metal isostatic pressing techniques. [78]

Hot Pressing

Temperature adequate for the hot pressing of tungsten powders are too great for the use of steel dies. Graphite dies are fairly satisfactory, but they suffer from the following disadvantages:

(1) Graphite die life is relatively short at the pressures and tenperatures required for hot pressing tungsten powders.

(2) Usually some contamination of the tungsten from the die occurs, and must be taken into consideration. The compact may require subsequent machining to remove carburized surface.

(3) Uniform heating of large dies by induction is difficult.

(4) For large production runs, hot pressing in graphite dies becomes too expensive.

Where graphite-die pressing is applicable, combined pressure-molding and sintering is feasible in one comparatively short time operation; closer dimensional control and higher final densities are possible. There also may be special cases in which graphite-die pressing is advantageous, for example, where the die
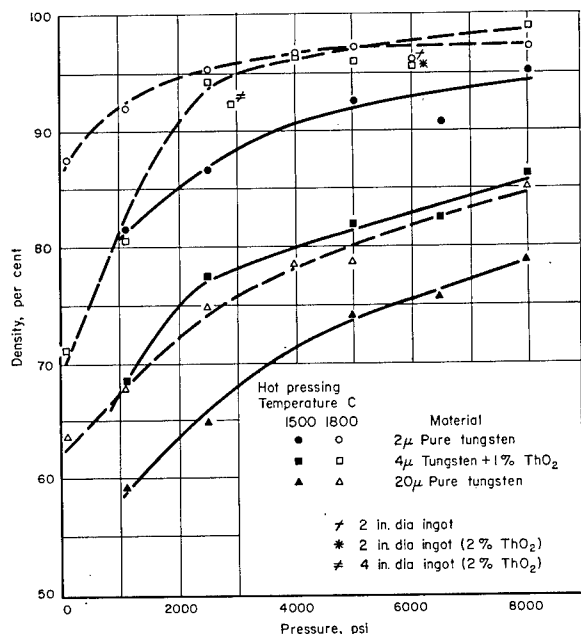
Figure 10.—Density-pressure relationship for hot pressing tungsten powder held 30 minutes at 1500° C and 1800° C.[83]

Figure 11.—Density-temperature relationship for hot pressing tungsten powder at 5000 psi.
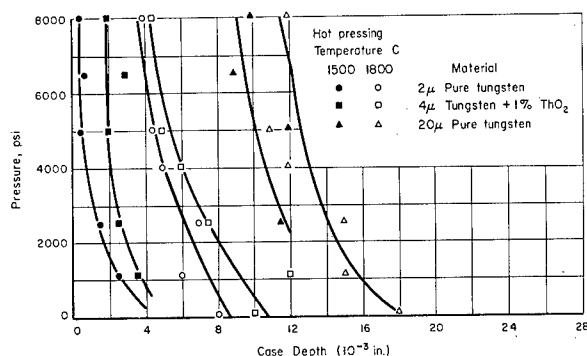
Figure 12.—Tungsten carbide case depth versus pressure for hot pressing tungsten powder at 1500° and 1800° C.[83]

remains as part of the finished shape, as in a composite nozzle structure.[80]

Graphite-die hot pressing has been described by Hoyt,[81] St. Germain and Slosarik,[82] and by White.[83, 84] Die and press designs for hot pressing refractory materials have been considered in detail by Jackson.[85] Figure 10 from White and Jurkowitz[83] illustrates the densities obtained in graphite dies in 30 minutes at two temperatures for various tungsten powders. Figure 11 illustrates the temperature-density dependence for a fixed compacting pressure. The carbide case depth formed on tungsten appears to be strongly dependent on particle size as shown in figure 12.

It was concluded in this work that densities above 95 percent can be obtained by hot pressing in graphite dies at temperatures from 1500° to 1800° C and at pressures from 5000 to 8000 psi for fine particle sizes (<5 microns) of either pure tungsten or thoriated powder. Results also indicated that there was little benefit to be obtained by going to higher temperatures or pressures. Hot pressing did not appear practical for powders coarser than about 20 microns in view of the low densities obtained (less than 85 percent). Where controlled interconnected porosity is desired, for example,

for transpiration cooled structures, hot pressing of coarse powders may be advantageous.

In the consolidation of refractory metal alloys (80W–10Mo–10Cb and 68W–20Ta–12Mo) from elemental powders, hot pressing at temperatures above 2100° C has been encouraging where all constituent powders are finer than about 5 microns.[84] The use of substantially coarser powders leads to alloy inhomogeneity, requiring a high temperature postpressing anneal.

A variation of hot pressing has been developed in the last few years, referred to as "gas pressure bonding." It has been used in consolidating a variety of metallic and ceramic powders as well as in making diffusion bonds in parts. Gas pressure bonding is essentially a technique for elevated temperature isostatic pressing using a gas as the pressure medium. Canned materials are heated and subjected to pressure in a high temperature autoclave. The equipment used has been described in reference (86).

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For the consolidation of tungsten powder, temperatures of 2100° to 3200° F, times of 0.5 to 4 hours depending on the mass of contained material, and pressures of 2000 to 15 000 psi are commonly used. The details for pressing tungsten powder into billets, diffusion bonding of tungsten foils, or preparation of nose cones from tungsten powder, depend on the end objective. Contamination inherent in graphite-die hot pressing is avoided in the gas pressure bonding technique. On the other hand, use of gas pressure bonding methods ordinarily makes necessary the removal of the container either by solution or by machining. References (87), (88), and (89) detail the bonding of tungsten powder, and reference (90) illustrates a bonded spherical tungsten product.

Sintering

The general behavior of tungsten powders during sintering has been studied for the past 50 years. The state of the art as of about 10 years ago has been discussed in detail by Agte and Vacek[7] and briefly summarized by Jones.[91] With the development of tungsten as a space hardware material, there has been a renewed interest in sintering in view of the fact that it is still and probably will continue to be the principal means of tungsten consolidation. This resurgence is illustrated, for example, by references (92) to (99) for the nonactivated, and by references (100) to (115) for the activated sintering of tungsten. There has been no comprehensive study of data from various investigators in order to arrive at a generally applicable metal powder sintering theory. As a matter of fact, there is some disagreement among powder metallurgists concerning the exact meaning of the term "sintering" itself.[116] Kothari[95] examined data from a number of sources and concluded that "in general, all the results, experimental and theoretical, support the idea that grain boundary diffusion is the predominant mechanism of material transport during the sintering of tungsten in the temperature range of 1100–1500 C." For coarse particles in the range 14 to 16 microns surface diffusion appears to be the dominant operative mechanism during sintering.[99] At the present time, it appears that densification of tungsten powder compacts during sintering is sufficiently dependent on the properties of individual

powder types and sintering schedules, that predictions of rates cannot go beyond approximations. However, data from some of the references cited should be of interest in this regard.

According to Matt,[187] for tungsten powders of any particular particle size and sintering temperature, the maximum density will be nearly reached within the first hour of time. Additional sintering time will only tend to round pore passages, with consequent removal of notch effects and an increase in strength.

As a rule, temperatures at which the onset of densification of metal powders becomes significant are about $0.3T_m$–$0.45T_m$, where T_m is the melting temperature in degrees absolute. For tungsten, this temperature is $0.40\ T_m$ according to Hüttig, as noted in reference (117). Normally, sintering is carried out at temperatures in excess of at least $0.6\ T_m$. In a high melting temperature metal such as tungsten, there is an unusual incentive to resort to some sort of "activated" sintering, in which case the desired densities can ordinarily be achieved at lower sintering temperatures. For example, Brett and Siegle[111] have found that clean tungsten wire surfaces in contact will not bond below 1600° C, but, in the presence of even very small amounts of nickel (0.00001 in. of electroplate on 0.001 in. tungsten wire), bonding and neck growth occurred at a temperature as low as 1050° C. In work described in reference (115), bromine atmosphere activation was found to occur between 1200° and 1700° C, with an activity maximum at about 1400° C, at which temperature densification was increased by 40 percent.

The overriding factor determining strength in a tungsten powder shape that has not reached full density (and ordinarily 100 percent full density cannot be reached by sintering alone) is the amount of porosity. The effect of porosity on mechanical strength has been critically reviewed by Knudsen[118] who found that the relation between the strength S, the porosity P, and the grain size G of a porous sintered metal powder or ceramic body can be approximated by equations of the form

$$S = kG^{-a}e^{-bP}$$

where k, a, and b are empirical constants. In earlier work on the strength of slip-cast tung-

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sten, the empirical relationship $S=86,000e^{-3.67P}$ was observed.[119] In general, the drop in strength for any particular difference in porosity between two as-sintered specimens is greater in the high density than in the lower density ranges.

Tables XIII, XIV, XV, and XVI summarize mechanical properties data from a series of measurements on porous tungsten.[120] The general conclusions reached as the result of this work were as follows:

(1) A large scatter in mechanical property data of pressed-and-sintered tungsten of 85, 90, and 95 percent of theoretical density can be attributed primarily to the variations in processing schedules and powder lots used by the material suppliers.

(2) Ductility, as measured by percent elongation and percent reduction of area, was determined to be inversely related to strain rate and directly related to percent theoretical density.

(3) The tensile properties of pressed-and-sintered tungsten are strain rate dependent. Relative brittleness at the lower temperatures prevented the establishment of consistent quantitative trends.

(4) The scatter in data for modulus at various strain rates below 1000° F precludes any evaluation; however, within the rate range investigated, the modulus should be insensitive to strain rate variations.

(5) The creep rate (up to 0.001 in strain) becomes progressively sensitive to temperature and is somewhat insensitive to stress in the temperature range of 2000° to 5000° F.

(6) The creep behavior of pressed-and-sintered tungsten does not appear to be influenced by variations in percent theoretical density in the range investigated.

The data presented in tables XIII to XVI are not valid for use in detailed design work, but are of value in illustrating gross trends.

The critical study by Jenkins[117] should be checked for a general summary of the effect of porosity on sintered metal powder bodies.

Explosive Compaction

Explosive compaction of tungsten powder to yield high densities is feasible, but, at the present time, has not found wide application. Explosive compaction of metal powders will most likely find application in those areas which require either large or complex shapes, that

Table XIII.—Mean Tension-Test Results on Pressed-and-Sintered Tungsten of 85% Theoretical Density

Temperature, ° F	Strain rate, in./in./min	0.2% offset yield strength, 10^3 psi	Ultimate tensile strength, 10^3 psi	Elongation in 1.0 in., %	Reduction of area, %	Modulus of elasticity, 10^6 psi	No. of data points
Room	0.017	(a)	58.4	0.0	0.0	20.8	4
500	0.017	(a)	55.3	0.0	0.0	18.3	4
500	0.1	(a)	43.0	0.0	0.0	30.0	4
1000	0.005	(a)	51.0	0.0	0.0	47.0	2
1000	0.017	(a)	47.6	0.0	0.0	17.0	4
1000	0.1	(a)	55.0	0.0	0.0	32.6	3
1000	10.0	(a)	42.9	0.0	0.0	53.5	2
1500	0.017	37.9	38.0	1.2	2.6	15.5	2
2000	0.017	29.7	30.0	2.0	2.7	14.0	3
2000	0.1	39.5	42.0	4.8	6.5	39.0	2
3000	0.017	16.9	17.4	4.4	12.9	9.5	3
3000	0.1	21.6	22.2	7.8	24.6	32.0	3
3000	10.0	16.9	34.2	13.2	46.2	36.0	1
4000	0.017	6.8	7.5	11.5	15.3	3.2	3
4000	0.1	10.2	11.0	5.4	23.6	10.0	2
5000	0.017	2.8	3.1	6.5	11.5	1.3	2
5000	0.1	4.0	4.1	5.2	12.0	1.8	1
6000	0.017	0.6	0.8	12.4	25.0	0.2	1

(a) Specimens failed before 0.2% offset yield.

Table XIV.—Mean Tension-Test Results on Pressed-and-Sintered Tungsten of 90% Theoretical Density

Temperature, °F	Strain rate, in./in./min	0.2% offset yield strength, 10^3 psi	Ultimate tensile strength, 10^3 psi	Elongation in 1.0 in., %	Reduction of area, %	Modulus of elasticity, 10^6 psi	No. of data points
Room	0.017	(a)	53.3	0.0	0.0	40.8	3
500	0.005	(a)	34.8	0.0	0.0	54.5	2
500	0.017	(a)	39.4	0.0	0.0	40.4	5
500	0.05	(a)	40.1	0.0	0.0	51.0	2
1000	0.005	47.9	50.0	3.2	3.9	45.5	2
1000	0.017	35.8	39.6	2.4	2.0	34.2	10
1000	0.05	(a)	59.3	0.0	0.0	52.0	2
2000	0.017	28.7	36.4	6.9	16.0	21.6	9
2000	0.05	23.9	30.9	9.7	18.8	38.5	2
2000	0.1	22.9	29.2	4.8	19.1	37.5	2
3000	0.017	18.0	20.5	8.8	31.0	19.6	6
3000	0.05	18.8	19.8	7.2	24.8	26.0	2
3000	0.1	22.3	22.3	6.3	25.6	35.0	1
3000	10.0	31.7	43.4	12.0	23.1	47.0	1
4000	0.017	9.2	9.7	9.8	43.0	(b)	1
5000	0.017	2.3	2.8	8.8	13.5	1.7	2
6000	0.017	0.7	0.7	10.6	33.0	0.6	1

(a) Specimens failed before 0.2% offset yield.
(b) Modulus not measurable from stress-strain curve.

Table XV.—Mean Tension-Test Results on Pressed-and-Sintered Tungsten of 95% Theoretical Density

Temperature, °F	Strain rate, in./in./min	0.2% offset yield strength, 10^3 psi	Ultimate tensile strength, 10^3 psi	Elongation in 1.0 in., %	Reduction of area, %	Modulus of elasticity, 10^6 psi	No. of data points
Room	0.017	(a)	61.0	0.0	0.0	44.5	1
500	0.005	(a)	36.4	0.0	0.0	62.0	2
500	0.017	(a)	52.5	0.0	0.0	37.6	4
500	0.1	(a)	44.7	0.0	0.0	42.0	2
500	10.0	(a)	46.1	0.0	0.0	54.0	1
750	0.005	(a)	44.8	0.0	0.0	52.0	1
750	0.1	(a)	44.8	0.0	0.0	48.0	2
750	10.0	(a)	33.2	0.0	0.0	45.5	2
1000	0.005	37.7	51.1	10.7	17.2	29.5	2
1000	0.017	41.0	48.0	9.9	28.9	34.8	2
1000	0.1	38.4	54.8	9.9	28.9	25.5	2
1000	10.0	(a)	52.1	0.0	0.0	50.0	2
2000	0.017	17.8	33.6	31.5	51.5	22.7	3
2000	0.1	24.4	41.2	32.1	59.5	21.5	2
3000	0.017	13.0	20.5	16.8	39.5	13.0	3
3000	0.1	22.7	24.2	24.3	58.5	15.0	2
4000	0.017	8.6	8.9	8.5	13.6	4.2	3
4000	0.1	10.0	11.1	7.3	15.8	17.0	2
5000	0.017	4.9	5.0	8.0	17.0	2.0	1
6000	0.017	1.1	1.2	14.0	15.5	0.4	2

(a) Specimens failed before 0.2% offset yield.

Table XVI.—Pressed-and-Sintered Tungsten Creep-Rupture Properties

Test temp, °F	Stress, psi	Time, in minutes, to elongate				Creep elongation		Average strain rate to 0.1% elongation, %/sec	Density, % of theoretical
		0.1%	0.5%	1.0%	Rupture	4 min	At rupture		
2000	26 800	1.3	---------	---------	---------	0.20	---------	0.0014	92.5
2000	26 800	3.5	---------	---------	---------	0.11	---------	0.0005	93.2
2000	16 800	4.0	---------	---------	---------	0.10	---------	0.0004	95.3
3000	19 000	0.02	0.04	---------	0.04	---------	0.50	0.0833	84.0
3000	19 000	0.02	0.38	0.72	1.32	---------	8.58	0.0833	85.0
3000	11 900	0.12	---------	---------	0.26	---------	0.77	0.0139	84.4
3000	11 900	0.29	2.32	---------	---------	0.77	---------	0.0051	85.5
3000	9 500	0.320	2.144	---------	---------	0.79	---------	0.0052	90.0
4000	7 780	0.003	0.012	0.024	0.215	---------	8.90	0.5555	90.0
4000	4 970	0.019	0.99	2.03	3.35	---------	2.57	0.0087	95.3
4000	3 100	0.01	0.05	0.08	0.12	---------	2.32	0.1666	84.9
4000	3 100	0.15	0.85	1.98	---------	1.85	---------	0.0111	93.8
5000	3 010	0.006	0.030	0.070	0.100	---------	1.67	0.2777	90.0
5000	2 330	0.020	0.086	0.169	0.401	---------	4.00	0.0833	87.6
5000	2 040	0.05	0.24	0.45	0.56	---------	1.89	0.0333	92.6
5000	1 880	0.140	0.610	0.946	2.055	---------	6.05	0.0119	90.0
5000	1 270	0.06	0.43	1.45	---------	2.10	---------	0.0277	95.8

would be impractical to compact by more conventional powder metallurgy techniques. In experimental work with tungsten powders, "green" densities as high as 95 to 97 percent have been achieved.[121,122] According to calculations in a Soviet paper, during the shock compression of porous tungsten, exceptionally high temperatures (up in the 20 000 to 30 000 K range) may be reached momentarily.[123]

Powder Rolling

Tungsten powder can be consolidated by rolling in an appropriate sheath or can.[124] From a practical standpoint, however, this is of less interest than the cold compaction and sintering by direct rolling. The first effort toward the direct rolling of tungsten strip from powder is represented by a German patent in 1902 (DRP 154 998, Nov. 14, 1902).[125] In a more recent work, it was possible to roll tungsten powder directly into a weak but manageable strip.[126] Further success was encountered in Los Alamos work.[127] A horizontal mill was used to permit vertical feeding into the compacting rolls. Tungsten powders varying from 1 to 10 microns average particle size were tested for rollability. Powders of 3 microns

and less average diameter did not roll well. Coarser powders tended to cohere well and yielded higher as-rolled densities. The best combinations of thickness and density appeared to result from powders of high bulk density compacted at 1 fpm, with roll openings of 10 mils and a powder head as high as possible (that is, up to 4 inches). Maximum thicknesses attained in 2½-inch-wide strip were in the range 60 to 68 mils with green and sintered (1700° C, 3090° F) densities about 80 to 85 and 90 to 95 percent, respectively. Lamination tendencies were not encountered until thicknesses near 70 mils were reached. Strips several feet in length were rolled. Mixtures of W with UO₂ could be rolled successfully. In later, related work[128] on the flow of tungsten powder into roll gaps, it was shown that atmospheric humidity greatly affects the flow characteristics of the powder. The humidity effect may depend strongly on the type of powder and on the powder particle size.

Other efforts to roll tungsten powder into sheet was reported by Ang, but no data were given.[129] A cyclic process for the compaction of tungsten into strip has also been described.[130]

Extrusion of Powder

Extrusion of a tungsten powder-binder mixture is not a new concept, having been used in filament manufacture earlier. There has been a recent suggestion that extrusion of tungsten powder-binder mixtures may be a useful way of making larger shapes.[131] Tungsten powder alone is not well adapted to direct extrusion at ambient temperatures. However, there are indications that tungsten powder can be hot extruded to yield rod and tubing.[132,133]

Vapor Deposition

The buildup of tungsten free-standing forms and the deposition of tungsten coatings for hardware, for example, the facing of graphite nozzle throats, have been reported. In the case of tungsten, three categories of reactions are of interest:

(1) Pyrolysis of organo-metallic compounds of tungsten, for example, $W(CO)_6 = W + 6CO$

(2) Thermochemical reduction of tungsten halides by means of a gaseous reducing agent, for example, $WX_6 + 3H_2 = W + 6HX$, where X is a halide

(3) Pyrolysis of a tungsten halide, that is, $WX_6 = W + 3X_2$, where X is a halide.

For forming free-standing structures, for example, nozzle shapes or tubing, reaction 2 is used extensively.[134] The halide most commonly used is WF_6. This material recently has been made available in very pure form. The chloride has also been used for this purpose.[135] Use of the fluoride provides greater purity of deposit and simplifies the deposition process by eliminating the need for evaporators or further purification.

An important advantage of vapor-deposited tungsten is the exceptionally high purity obtainable, as illustrated in table XVII.[136] The process is controllable through well developed chemical engineering procedures. The deposits are readily machined. Joining by diffusion bonding is ordinarily preferable to welding, which results in a cast structure. A major advantage of vapor-deposited tungsten is its resistance to grain growth. This resistance appears to be related to the characteristic low-angle grain boundaries and the absence of strain-related stored energy, both of which would encourage grain growth. Numerous tests have been conducted at 1800° C up to 1200 hours with no observable change in grain diameter. Other, shorter time tests at temperatures up to 2500° C have also indicated remarkable resistance to grain growth.[137]

Table XVII.—Typical Purity of Vapor-Deposited Tungsten [136]

Element	Concentration, ppm	Element	Concentration, ppm
O$_2$	<10	Mg	0.5
N$_2$	<15	Mn	N<0.5
C	6–10	Mo	N<100
H$_2$	2–4	Na	N<20
F	5–10	Ni	N<1
Ag	N<0.5[a]	Pb	N<4
Al	N<1	Rb	N<2
As	N<20	Sb	N<6
B	N<4	Si	<2
Ba	N<2	Sr	N<20
Ca	N<10	Te	N<200
Cd	N<8	Th	N<80
Co	N<1	Ti	N<6
Cu	N<0.5	Tl	N<8
Fe	<1	V	N<8
Hg	N<8	Zn	N<20
In	M<20	Zr	N<20

(a) N=not detected. In these cases, the lower limit of detection by conventional spectrographic techniques is indicated.

In tensile tests from 1370° to 2980° C, vapor-deposited tungsten displayed lower strengths than wrought powder metallurgy tungsten due in a large part to void formation.[138] Other studies have shown that, where void formation does not occur, the high-temperature properties of vapor-deposited tungsten are quite similar to those of wrought material.[136]

Vapor deposition has also been useful in nuclear metallurgy.[139,140] Additional information dealing with vapor deposition of tungsten is contained in references (142–151).

As is the case with plasma spraying, vapor deposition as a process is applicable under special conditions where less expensive processes will not yield the required product.

Plasma-Arc Deposition

Investigation of tungsten metal spraying as a method of building up rocket nozzle throat shapes was begun about 1958 at a time when combustion temperatures of newly developed

aluminized solid propellants exceeded 5000° F. Because tungsten was difficult to fabricate by conventional methods, flame spraying seemed to offer an ideal method of forming nozzle hardware or of building up other solid tungsten bodies. It was concluded in the final report on this work [152] that:

(1) The plasma (powder) spray process provides a stronger tungsten deposit than does the arc (wire) spray process.

(2) Plasma spraying of tungsten in a controlled environment offers strength and purity advantages over spraying in air.

(3) Activated sintering by alloy additions is feasible for improving strength and density of sprayed tungsten.

(4) Sprayed tungsten rocket nozzles functioned satisfactorily for firings at moderate chamber pressures ($\sim$600 psi); at higher pressures, erosion was encountered.

Arc-plasma devices are the only practical means of producing and maintaining extremely high temperatures for the spraying of high melting metal powders. Table XVIII illustrates the comparative position of the arc-plasma with respect to other heat sources from the standpoint of temperature, stream velocity, and rate of heat transfer. The power requirements of any arc-plasma device depend on its particular use, but 10 to 100 kw is sufficient for spheroidizing, spraying to consolidate, and the manufacturing of ultrafine metal powders.

The arc-plasma jet spraying of tungsten has been covered in detail in a number of places [154-171] and, therefore, will not be described in detail here.

A variety of deposits can be made by the plasma spraying of tungsten powder. These include thin, high-quality impervious coatings, thick high-quality and relatively void-free deposits, deposits of varying thickness which may contain intentional or unintentional voids, and thick deposits such as forging blanks which may be subsequently mechanically worked to produce a wrought structure. It is also possible, for example, to make graded deposits. Arc-plasma spraying of tungsten is often a very good method for making irregular shapes that would be difficult to produce by some other procedure.

The properties of as-sprayed materials are adequate for many applications, but there are occasions when maximum attainable strength or some other particular property is required. Strength properties in as-sprayed tungsten are commonly improved by a postsintering operation as described by Brophy et al [168] and Singleton. [170]

A substantial contribution to the understanding of sprayed deposit-substrate bondings is represented by NASA work, principally that of Grisaffe and Spitzig. [158-160, 162, 164] In their work, during spraying of tungsten powder on a molybdenum surface, coating-to-substrate bonding occurred when the substrate was preheated to 2200° F or higher. The metallugrical bond resulted from the growth of substrate grains into the tungsten coating. The molybdenum substrates were completely recrystallized even though the total time for preheating, spraying, and cooldown to 400° F was only about 30 seconds. In spraying tungsten on a tungsten substrate, it was found that metallurgical bonds could be effected below the substrate recrystallization temperature.

Pressureless Consolidation

Loose powder sintering has been used to consolidate beryllium powder to densities as

Table XVIII.—Approximate Comparison of Heat Sources [153]

Type of heat source	Temp., °C	Velocity, ft/sec	Heat transfer rate to object in flame, Btu/in.² sec
Air bunsen flame	1,650	20	0–5
Oxy-acetylene welding flame	3,100	400	5
Arc-plasma jet	5,500	1,800	45
Welding arc	11,000	20	70
Transferred constricted arc	22,000	15,000	250

high as 95 to 98 percent of theoretical.[174] Vibratory compacting has been used to compact various metal powders.[175-177] A third process of pressureless forming, slip casting, is the only one of current technological interest as far as tungsten is concerned.

The principal advantage of tungsten powder slip casting as compared to many other fabrication procedures lies in its relative ease of production and low cost. It is, in general, applicable for small production runs of complex shape having thin walls. Thick sections, or sections too large to be self-supporting on removal from the mold, or shapes to be extensively deformed mechanically, are usually not adaptable to slip casting production.

The slip making process utilizes three basic materials: a powder, a liquid suspending agent, and, normally, an additive which helps to maintain a stable suspension. The most useful deflocculants appear to be the ammonium and sodium salts of alginic acid.

The preparation of a tungsten powder slip for casting a box shape is illustrated by a General Dynamics report,[178] as follows.

(1) The 4-percent ammonium alginate solution is mixed at least one day before it is used. Distilled or deionized water is recommended for use in preparing the Marex solution.

(2) The ammonium alginate solution and tungsten powder are mixed in a Waring blender.

    (a) A slip ratio of 10:1 is obtained with 2500 grams of tungsten powder and 250 cc of alginate solution. The ratio may be increased according to the viscosity of the slip after it is mixed.

    (b) The entire amount of ammonium alginate solution is poured into a beaker and the tungsten powder slowly added while hand stirring until the mixture becomes reasonably flowable. Less than one-half of the powder will have been consumed at this point. The contents of the beaker are then poured into the blender. This method is preferred over complete mixing in the blender because it avoids excessive splashing of the binder which may retard accurate blending.

    (c) Ammonium hydroxide is added to the slip while blending, at the rate of one drop for every 100 grams of powder to be used in the slip.

    (d) The remainder of the powder is slowly added to the slip while blending.

    (e) The mixture is allowed to blend for several minutes after the powder has been added to assure complete dispersion of the powder.

    (f) The mixture is poured into a beaker and the viscosity and pH checked. The average viscosity should be approximately 8000 cps and the pH should be 6.0 to 7.0.

    (g) The slip ratio and viscosity may be adjusted at this point. If the viscosity is low, powder is added to the slip. If the viscosity is high, additional blending may drop it to the proper level. Otherwise, binder will have to be added to the slip to lower the viscosity.

(3) The slip is poured into a filter flask and vacuum deaerated for 30 seconds.

Vibration was applied to the plaster mold during pouring and for 4 hours after, or until shrinking had virtually ceased. Additional slip was fed into the mold to make up shrinkage during consolidation. The casting was allowed to solidify over night before removal. This particular work was part of our effort to densify slip-formed or plasma-sprayed shapes by HERF (high energy rate forming). This effort to work the slip-formed and plasma-sprayed shapes proved impractical in both cases.

Further details of the slip-casting process applicable to tungsten powders are available in references (172), (173), (179), (180), (181), (182), and (183).

Infiltration

The infiltration of porous tungsten skeletons to yield a composite structure has been in use for some time in the production of electrical contacts.[184] Kieffer and associates, in a general discussion on infiltration, note a 1916 patent covering porous tungsten-silver or -copper infiltrated composites.[185] The problem of achieving complete infiltration is magnified in the transition from contact materials to porous tungsten sweat-cooled nozzle hardware. The empirical rules from Kieffer[185] for the pro-

duction of infiltrated structures (table XIX) illustrate the factors which should be considered in the infiltration of any large object. In the case of a porous tungsten nozzle preform, the principal problem is in getting a form completely receptive to the infiltrant. Commonly, for a preform approximately 80 percent dense, the efficiency of silver infiltration is about 90 percent.[186] Major defects in the pressed-and-sinterd body are gross porosity, flash-sintered fines, and chemical contamination.[187] Flash sintering may occur in areas within the pressed shape where there is a disproportionately large concentration of tungsten fines (particles of average diameter less than about 2 microns). This results in localized high density areas with associated gross porosity. Closer processing control is helpful in reducing the incidence and severity of these defects. Figure 13 illustrates a properly infiltrated structure.[188] The processing schedule required to produce any specified structure will vary with the characteristics of the starting tungsten powder. Table XX[189] illustrates the density and interconnected porosity obtained in a particular set of experiments. Calculated pore sizes are listed in table XXI.[189] Processing details are discussed in references (190) to (192). A theoretically based index of infiltration of general applicability has been developed by Shaler[193] on the basis of thermodynamic considerations.

Infiltration of tungsten is of particular importance in the production of sweat-cooled nozzles.

STRUCTURES

Tungsten as a structural material for vehicle hardware is characterized by specialized applications. In general, it is used in, but is not restricted to, cases where high temperature strength requirements exceed those that can be provided by lower melting metals, for example, as a backing plate to withstand reentry stagnation temperatures. The following sections illus-
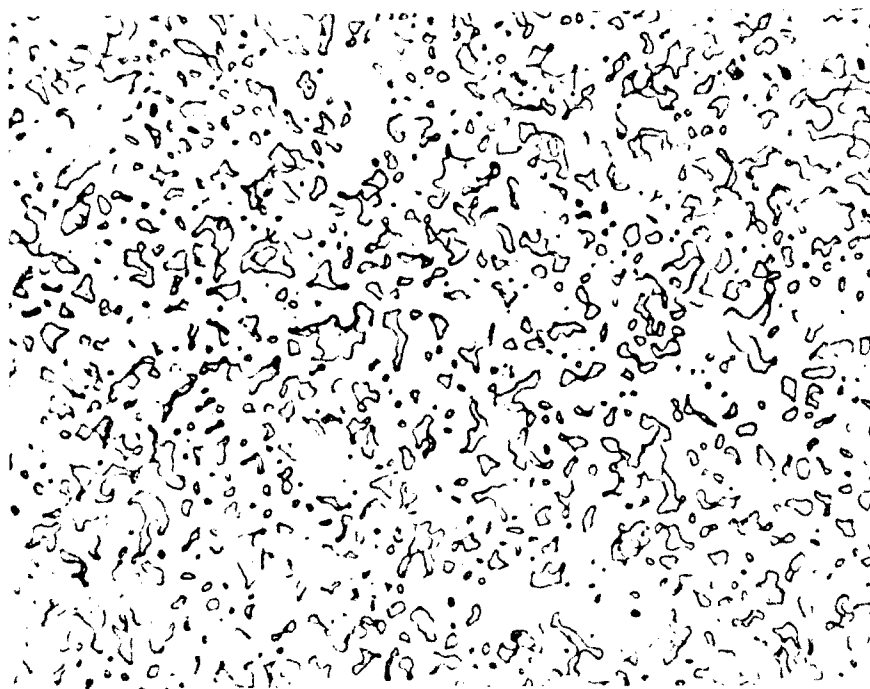
Figure 13.—This photomicrograph, taken at 500 X from an unetched specimen, shows the silver evenly dispersed throughout the tungsten matrix.

Ultimate tensile strength:		Density	16.80–17.76 g/cc
Minimum	50 000 psi	Electrical conductivity	Approx. 33% IACS
Typical value	75 000 psi	Grain size, ASTM	10–12

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Table XIX.—Working Rules for Production of Infiltrated Structures

1. There should be a marked difference between the solidus temperature of the skeleton and the infiltration temperature of the liquid.
2. The mutual solubilities of the components at room temperature should be as low as possible. Any significant solubility should occur only at higher temperatures.
3. The development of any eutectic, solid solution, or intermetallic phase which would impede the capillary advance of the infiltrant by means of a volume increase, or by an increase in the fluid viscosity of the infiltrant, should be avoided.
4. The infiltration temperature should be just above the liquidus of the infiltrant in order to minimize mutual solution.
5. Where interference by metallurgical reactions may occur, the infiltration time should be held to a minimum.
6. The presence of non-wettable oxide films should be avoided either by preventing their formation or by their removal prior to infiltration.
7. Infiltration in vacuum should be employed for systems exhibiting poor wetting characteristics. Even under unfavorable conditions, this may practically eliminate residual porosity.
8. Skeleton and infiltrant metals forming oxides which are not reducible by hydrogen should be introduced in pre-alloyed form.
9. In cases where the infiltrant is an alloy, it is advantageous to use an alloy composition in equilibrium with the skeleton at the infiltration temperature. Infiltrants exhibiting significant solubility for the skeleton can be used in the form of presaturated alloys.
10. Where any phase has a low boiling point, it may be necessary to infiltrate in a closed container under pressure.
11. If diffusion or annealing treatments are carried out subsequent to infiltration, they should be performed at temperatures below the melting point of any liquid phase, and possibly under pressure.
12. In the case of systems which alloy readily, complete infiltration can be achieved if skeletons with very large pores are used and the infiltration time is kept to a minimum.
13. The use of fluxes of one kind or another may facilitate wetting and infiltration when oxide films are present.
14. The infiltration process can be facilitated by adding to the skeleton interior auxiliary metals which alloy with both components.

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trate the application of tungsten powder metallurgy to hardware. In the example of ion rocket engines, the superior contact ionization efficiency of cesium on tungsten as compared to that on molybdenum, tantalum, or rhenium, is important.[240]

Infiltrated Nozzle Materials

The premium for high combustion temperatures in rocket engine operation is illustrated by the relation between specific impulse and combustion chamber (fig. 14).[194] The most severe consequent temperature and abrasion problem commonly occurs at the throat section. Where throat dimensions must be closely maintained, tungsten is commonly used as the liner material at the constriction zone. With rising engine temperatures, the advantage of cooling is obvious. Various cooling procedures have been discussed in detail by Steurer,[195] and will not be considered here. From a gross design weight per unit area of surface, at very high heat fluxes, transpiration (or sweat cooling) is preferable to practically all other types. As early as 1942, a patent was filed for the injection cooling of a nozzle.[196] Sweat-cooling of turbine engines was discussed in detail in a 1952 paper.[197] The adaptation of porous tungsten for this purpose is the result of considerable developmental work.

Table XXII lists some possible infiltrants to function as coolants during firing. Although some other metals appear preferable on the basis of heat absorption per unit volume (last column), silver is currently the preferred coolant for a number of reasons, including ease of infiltration, compatibility with tungsten, and adequate vapor pressure at exhaust temperatures. Figure 15 is a schematic representation of heat absorption in the case of silver infiltrated tungsten. The preparation of an adequate tungsten preform is necessary both for the reception of infiltrant during fabrication and for adequate boil-off rates during firing. For these reasons, optimum permeability of the tungsten preform must be built into the cooled structure. Numerous permeability studies have been made for this purpose. In NOTS work

Table XX.—Effect of Powder Size, Compaction Pressure, and Sintering Temperature [a] on Sintered Porosity of Tungsten [186]

Powder		Compaction pressure, ksi	Sintering temperature, °F	Porosity, %	
Size, microns	Shape			Bulk	Intercon-nected
7. 6	Irregular_____	10	4000	30	30
		20	4000	26	26
		25	4000	23	23
		25	4500	16	13
		40	4000	19	17
		50	4000	17	15
		50	4500	10	4
4. 1	Irregular_____	10	4000	16	12
		25	4000	12	5
		40	4000	10	1
		50	4000	10	1
10	Spherical_____	10	4000	27	26
		10	4500	16	15
		25	4000	24	22
		25	4500	14	12
		40	4000	20	18
		40	4500	12	8
		50	4000	19	17
		50	4500	11	6
20	Spherical_____	10	4000	30	30
		25	4000	27	27
		25	4500	27	27
		50	4000	22	22
		50	4500	22	22
30	Spherical_____	10	4000	33	33
		25	4000	30	30
		25	4500	29	29
		40	4000	25	25
		50	4000	23	23
		50	4500	23	23

(a) Pressed compacts presintered in dry hydrogen for 6 hours; final sintering in vacuum for 4 hours at the temperature noted.

(ref. 198), Robinson found the permeability, K, of tungsten powder compacts to be related to porosity ϕ by the expression

$$K = \alpha \phi^n$$

where n is a porosity coefficient equal to 4.38 and α is a variable whose value is dependent on the characteristics of the powder in the particular compact. Strengths of infiltrated tungsten throats are ordinarily increased by increased densification of the tungsten matrix preform. At the same time, this reduces the total pore volume available for coolant storage, and also the permeability. An optimum density appears to lie in the vicinity of 80 percent.

Pertinent thermal shock studies, noted in references (201) and (202), have been made on both infiltrated and fully dense tungsten nozzle liner structures.

A current program has as its objective the development of the powder metallurgy and infiltration technology necessary for producing controlled porosity skeletons for fabrication as rocket nozzle inserts to operate in temperature environments as high as 7000° F.[203] A general analysis of the cooling process in infiltrated nozzle inserts during engine firing has been given by Gessner et al.[204]
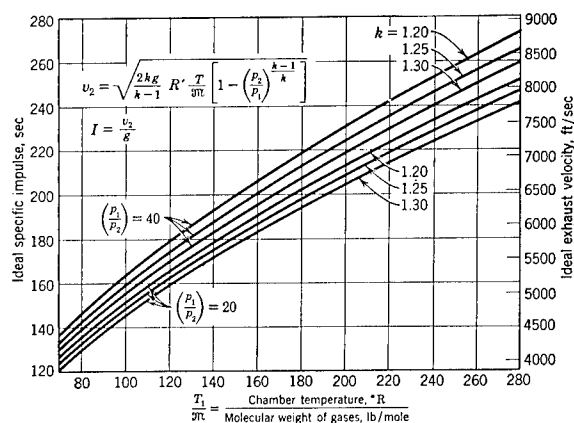
Table XXIII[205] illustrates the type of data obtained in studies on the properties of silver

Table XXI.—Low-Pressure Gas-Flow Pore-Size Determinations for Sintered Tungsten Matrices [189]

Initial powder		Interconnected porosity, %	Calculated pore size, microns
Size, microns	Shape		
7. 6	Irregular	23	7. 4
7. 6	Irregular	17	2. 9
10	Spherical	12	2. 9
10	Spherical	6	2. 1
20	Spherical	27	5. 4
20	Spherical	22	3. 3
30	Spherical	27	13
30	Spherical	23	6
80	Spherical	30	34
80	Spherical	24	24

infiltrated and copper infiltrated nozzle material. The following tentative conclusions were reached following an examination of the data.

1. The variation in properties measured for several vendors' products ranged up to 50

$$v_2 = \sqrt{\frac{2kg}{k-1} R' \frac{T}{\mathfrak{M}} \left[1 - \left(\frac{p_2}{p_1}\right)^{\frac{k-1}{k}} \right]}$$

$$I = \frac{v_2}{g}$$

$$\left(\frac{p_1}{p_2}\right) = 40$$

$$\left(\frac{p_1}{p_2}\right) = 20$$

$$\frac{T_1}{\mathfrak{M}} = \frac{\text{Chamber temperature, }^\circ\text{R}}{\text{Molecular weight of gases, lb/mole}}$$

Figure 14.—Specific impulse and exhaust velocity as functions of the chamber temperature and the molecular weight for various values of k and p_1/p_2. [194]

percent variation and reflects the state of the art of infiltrated tungsten in 1961. The advances in the state of the art since that time have produced a markedly improved, reproducible product. The strength properties obtained in the program are, therefore, not representative of currently used material and should not be used directly for design purposes.

Table XXII.—Heat Absorption Above 77° F for Several Metals [a]

Metal	Heat absorbed in solid state, % of that absorbed up to 5000° F	To melting point, btu/lb	To include ΔH_m, btu/lb	To include ΔH_v, btu/lb	To include vapor 5000° F, btu/lb	Btu/cu in. from 77° F to vapor at 5000° F
Ag	7. 7	105	153	1, 320	1, 360	517
Al	4. 7	286	459	5, 970	6, 080	592
Be	8. 6	1, 580	2, 140	18, 050	18, 300	1, 227
Ca	12. 0	296	385	1, 638	2, 530	142
Cd	4. 8	31	54	487	646	202
Cu	7. 4	198	286	2, 660	2, 690	870
Fe[b]	12. 1	453	570	3, 470		
Li	1. 9	260	446	11, 700	13, 500	256
Mg	8. 7	316	474	3, 010	3, 620	227
Mn	14. 1	373	508	2, 530	2, 650	715
Ni[b]	9. 6	348	477	3, 640		
Pb	3. 2	18	28	482	545	223
W[b, c]	10. 1	240	322	2, 370		
Zn	5. 8	71	120	981	1, 231	318
Zr[b]	8. 1	282	378	3, 480		

(a) References: Hultgren, R., Orr, R. L., Anderson, P. D., and Kelley, K. K., Selected Thermodynamic Properties of Metals and Alloys, Wiley (1963). Stull, D. R., and Sinke, G. C., Thermodynamic Properties of the Elements, Am. Chem. Soc. (1956).

(b) Vaporizes above 5000° F at 1 atmosphere, % to and including ΔH_v.
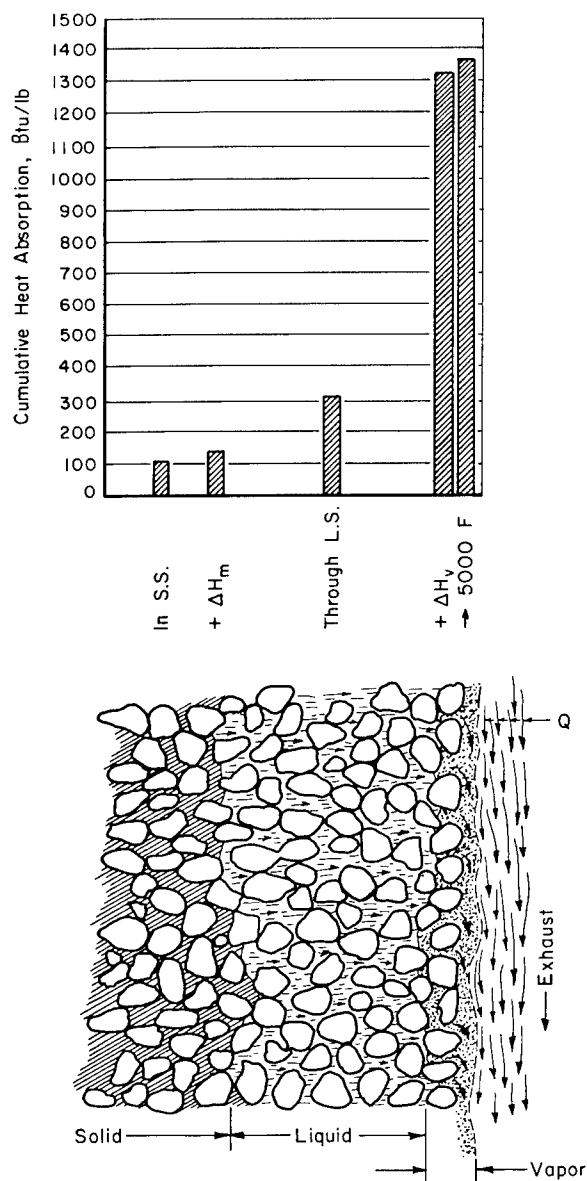
(c) Solid tungsten to 5000° F, 190 Btu/lb.

Cumulative Heat Absorption, Btu/lb

In S.S. +ΔH_m Through L.S. +ΔH_v 5000 F

Solid ——— Liquid ———

Vapor

Exhaust

Q

Figure 15.—Schematic representation of heat absorption by silver in an infiltrated tungsten nozzle liner wall.

2. The differences in strength levels observed for the two copper and the two silver infiltrated tungsten composites at a specified temperature in the range 700° to 3000° F are primarily attributed to the differences in percent-of-theoretical-density of the uninfiltrated pressed-and-sintered tungsten matrices, rather than to the presence of either infiltrant within the tungsten matrix.

3. The influence of the infiltrants on the mechanical behavior of the two copper and

the two silver tungsten composites manifests itself in two temperature ranges.

a. An apparent reduction in rotch sensitivity of the tungsten matrix and a resultant increase in the ultimate tensile strength attained is effected over the range 70° F to 700° F.

b. A decrease in ultimate tensile strength is observed over the range 3000° to 4000° F, which may be attributed to the presence of infiltrant vapors and their disruptive effects within the tungsten matrices.

4. An analysis of yield strength for the uninfiltrated as well as for all four composite materials as a function of test temperature reveals the following:

a. The activation energy governing the yielding process within the tungsten matrix of all four composites over the range 500° to 2500° F $\sim$11 400 cal/mole as compared to $\sim$24 600 cal/mole for the uninfiltrated tungsten.

b. The activation energy governing the yielding process in all four tungsten composites, as well as in the uninfiltrated tungsten, changes significantly over the range 2500° to 3500° F to a common one, $\sim$300 000 cal/mole for all five materials, and exhibits extremely high temperature sensitivity over the range 3500° to 4000° F.

5. The stress-dependence of the average creep rate to 0.001 in./in. strain decreases with increasing test temperature, approaching no dependence on applied stress for test temperatures greater than 3000° F.

6. The average creep rate to 0.001 in./in. strain of the uninfiltrated tungsten (85 percent theoretical density) is considerably more stress-dependent than that of the two copper infiltrated tungsten composites (64 and 78 percent theoretical densities).

7. The creep rate at a specified test temperature establishes a lower limit of tensile strain rate below which significant creep-unloading of the specimen will occur concurrently with tensile loading and modify the true tensile behavior.

8. The four infiltrated tungsten composites tested during this program do not manifest a sensitivity-to-strain rate over the range tested, 0.005 to 0.1 in./in./min.

The dynamic Young's modulus of tungsten-20 volume percent silver infiltrated material was evaluated up to 1020° C. Above 800° C,

Table XXIII.—Tension-Test Results on Pressed-and-Sintered Tungsten Infiltrated with 20 wt % Silver

Temp, °F	0.2% Offset yield stress, ksi	Ultimate tensile strength, ksi	Elongation in 1 inch, %	Reduction in area, %	Modulus of elasticity, 10^6 psi	Density of tungsten matrix, g/cc
Strain rate=0.005 in./in./min						
Room	(a)	52. 7	0. 5	0. 0	33. 3	12. 5
Room	(a)	69. 0	0. 0	0. 0	27. 9	12. 8
500	(a)	72. 3	2. 5	3. 5	35. 1	12. 9
500	(a)	56. 1	1. 5	0. 0	26. 7	12. 9
1000	(a)	49. 1	1. 0	1. 0	(b)	13. 0
1000	(a)	32. 1	0. 5	0. 2	(b)	13. 0
1000	(a)	19. 0	0. 2	0. 2	20. 7	12. 2
Strain rate=0.05 in./in./min						
Room	(a)	88. 5	0. 0	0. 0	31. 8	13. 1
Room	(a)	61. 5	0. 0	0. 0	32. 0	13. 1
Room	102. 0	102. 0	1. 7	0. 0	34. 0	13. 1
Room	(a)	70. 1	1. 2	0. 0	35. 2	12. 8
Room	(a)	68. 0	0. 0	0. 0	33. 5	12. 8
Room	(a)	38. 3	1. 2	0. 2	49. 0	12. 5
500	(a)	66. 8	0. 6	0. 0	27. 3	13. 1
500	(a)	55. 5	0. 6	0. 0	36. 0	12. 7
500	(a)	56. 6	0. 2	0. 0	34. 5	12. 8
1000	(a)	40. 3	0. 2	0. 0	30. 1	12. 8
1000	(a)	25. 4	0. 2	0. 2	21. 4	12. 3
1500	19. 6	21. 6	3. 2	1. 8	16. 1	13. 0
1500	20. 0	20. 5	2. 5	2. 0	23. 0	12. 7
2000	(a)	13. 8	0. 0	0. 0	10. 7	13. 0
2000	(a)	14. 5	0. 0	0. 0	16. 1	13. 0
2500	8. 8	12. 8	3. 2	6. 1	6. 2	13. 0
2500	(a)	6. 7	0. 0	0. 0	4. 4	12. 4
2650	3. 6	4. 8	2. 4	14. 4	(b)	----------
2700	4. 1	4. 1	2. 4	23. 2	5. 5	12. 4
3000	(a)	15. 3	0. 0	0. 0	10. 2	12. 7
3000	6. 9	6. 9	0. 8	2. 7	(b)	12. 8
3000	3. 0	4. 1	1. 6	4. 8	6. 2	12. 8
Strain rate=0.1 in./in./min						
Room	(a)	51. 8	0. 5	0. 0	29. 9	12. 8
500	69. 3	73. 4	1. 0	0. 0	24. 4	12. 8
500	(a)	40. 0	0. 0	0. 0	(b)	12. 9
1000	46. 8	49. 4	1. 5	0. 6	27. 1	12. 9
1000	(a)	47. 4	1. 0	0. 2	23. 2	12. 8
1000	(a)	25. 4	0. 2	0. 2	21. 4	12. 3

(a) Specimen failed prior to 0.2% offset yield.
(b) Modulus not obtainable from stress-strain curve.

the modulus decreased more rapidly than expected. Above the melting point of silver, the modulus of the composite structure was approximately equal to the modulus of a tungsten sample containing an equivalent percentage of pores.[206]

Reference (207) notes the infiltration of porous tungsten with copper and a copper-2 percent beryllium alloy. The age-hardened copper-beryllium alloy substantially increased the composite strength over that containing pure copper.

High Strength Composites

High strength composites in which embedded tungsten wire functions as a strengthening agent are of considerable interest as a way of reinforcing materials of lower elastic modulus and lower yield strength. A substantial fraction of the work to the present time, in which tungsten fibers have been used, has been carried out in National Aeronautics and Space Administration facilities.[208, 209, 212, 214, 218, 219, 220] Much of the work has been carried out on tungsten-reinforced copper in view of the practically insolubility of tungsten in copper. Some other fiber matrix combinations that have been studied are tungsten fibers plus aluminum oxide,[210] ceramic mixtures,[211] aluminum,[213] and, in work covered by reference (217), cobalt, cobalt alloy, and Nichrome. Reinforcement theory has been discussed in several papers, for example, references (219), (220), and (221). Strengths achieved by the incorporation of tungsten fibers in copper are illustrated by tables XXIV and XXV.[218] The composites were reinforced with either continuous or discontinuous fibers. The tensile properties and stress-strain behavior of composites reinforced with either type of fiber were similar, and, in both cases, the full strength of the fiber was utilized. The ultimate strength of the composites was found to be a linear function of the fiber content.

Tungsten Ionizers

The electrostatic acceleration or ion rocket engine is a propulsion candidate for distant space exploration. In principle, the thrust chamber incorporates an alkali metal vaporizing chamber, an ionization section, an accelerator

Table XXIV.—Tensile Strengths of Copper Composites Reinforced With 5-mil Tungsten Fiber [218]

Fiber, vol. %	Diameter, in.	Number of wires	Tensile strength, 10^3 psi
(a) Continuous reinforcement			
12. 6	0. 097	48	47. 7
15. 8	. 089	50	52. 0
16. 1	. 125	100	63. 5
27. 2	. 096	100	98. 3
27. 2	. 096	100	100. 1
28. 0	. 191	----------	97. 5
33. 6	. 122	177	102. 2
33. 9	. 113	172¼	122. 4
40. 2	. 093	139	137. 0
47. 7	. 117	261	154. 5
52. 7	. 113	267	189. 6
53. 6	. 123	325	182. 2
54. 4	. 095	197	188. 4
57. 2	. 118	317	178. 8
57. 3	. 121	338	189. 7
62. 4	. 124	372	210. 9
62. 7	. 077	150	215. 1
63. 5	. 121	369	213. 9
65. 0	. 112	325¼	225. 7
67. 1	. 122	400	231. 0
67. 4	. 119	385	228. 3
68. 1	. 117	371	227. 7
69. 2	. 108	323	235. 6
70. 2	. 108	326	238. 0
70. 2	. 085	204	238. 4
71. 6	. 118	399	242. 9
72. 4	. 083	200	238. 9
72. 9	. 110	356	239. 9
75. 4	. 127	483	249. 8
76. 8	. 087	231	254. 9
(b) Discontinuous reinforcement			
12. 4	0. 143	101	41. 1
14. 1	. 143	117	57. 3
14. 4	. 135	105	56. 6
18. 2	. 126	115	62. 6
21. 3	. 125	133	49. 0
23. 3	. 129	154	57. 7
25. 2	. 111	124	91. 1
27. 9	. 120	161	115. 8
32. 3	. 101	132	110. 0
32. 4	. 117	178	100. 3
35. 7	. 101	146	120. 0
36. 0	. 128	234	90. 3
37. 7	. 118	210	93. 5

Table XXV.—Modulus of Elasticity of Copper Composite Reinforced with Tungsten Fiber

Fiber, vol %	Modulus of elasticity, 10^6 psi
(a) Continuous reinforcement	
18.7	26.4
24.3	26.7
26.7	28.3
29.0	30.0
32.3	29.8
35.9	30.2
55.0	41.6
57.6	41.7
64.9	44.4
66.6	44.3
67.3	45.6
75.5	48.3
Copper	17.7
Tungsten	58.8
(b) Discontinuous reinforcement	
23.0	26.1
25.0	28.9
25.7	28.2
26.9	27.9

grid, and an electron emitter. It has been described in simple terms in a number of places, for example, in references (222–227). The greatest research and development work in the direction of producing an operable ion rocket engine has been carried on at National Aeronautics and Space Administration facilities or at other facilities under NASA contracts as illustrated by references (228–246). Some additional efforts are represented by references (247–249).

Tungsten performs a critical function in the ionization section of the engine, and, for that reason, much work has been done to develop a workable structure. The basic concepts of the contact-ionization thruster were first presented by E. Stuhlinger in 1954 and 1955.[250, 251] Studies of porous ionizers started with the application of porous tungsten in ion engines in late 1958. The general metallurgical requirements may be summarized as follows:[247]

1. Pore sizes in the submicron range

2. Pores available on approximately 5 micron center-to-center distances over the full emitter area
3. Long term dimensional stability of ±0.001 inch (at operating temperatures in excess of 2000° F for times in the order of 1 to 2 years)
4. Possibility of making reliable joints (brazing, welding, and so on) which are vapor tight, and which will not contaminate the emitter surface.

Woven wire cloth, finely spaced holes drilled in metal sheets, closely packed wire bundles, and sintered powder compacts made from both angular and spherical tungsten powders have all been investigated as ionizing structures.[239] It has been concluded that porous tungsten materials processed by powder metallurgy methods from spherical powder appear most satisfactory at this time. However, tungsten ionizers still remain a problem from a life standpoint. In a recent assessment, Mickelsen and Kaufman note:[243] "The performance of the contact-ionization thrustor is severely limited by porous-tungsten technology. The requirements for submicron, close-spaced pores without in-flight sintering appear formidable." Figure 16 from Mickelsen,[243] and earlier from
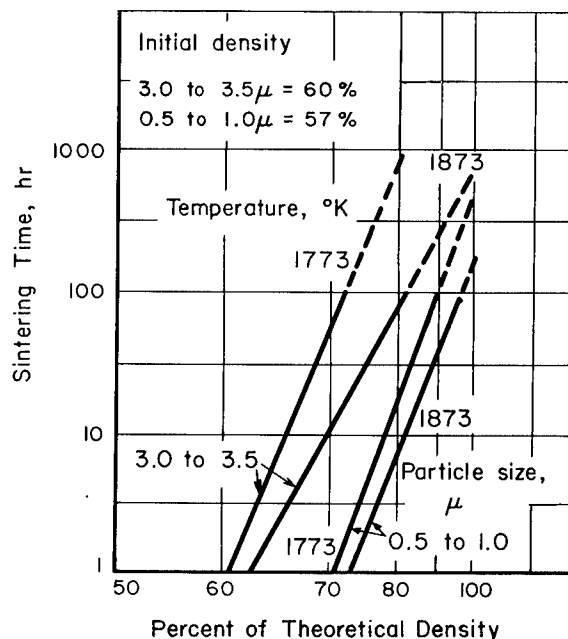

Figure 16.—Sintering rates of porous-tungsten ionizers. Compacting pressure, 34 000 pounds per square inch; atmosphere, dry hydrogen.[243]

Turk,[252] illustrates the tendency of porous shapes made from fine tungsten powders to continue sintering in service tests.

Recent efforts to produce an improved ionizer involve compacting and sintering studies on closely graded spherical tungsten powder to yield average pore sizes of 0.5, 1, 2, and 3 microns.[27] The use of angular powder for ionizer preparation has several disadvantages, including the difficulty of size classification of starting powders, accelerated sintering behavior, lack of uniformity of pore parameters, and insufficient product reproducibility. A second problem associated with porous tungsten ionizer development has been the general inability in the past of ion engine technology to accurately define and specify pore parameter requirements. Any future success in ion engine development depends very greatly on successful powder metallurgy development of the ionizer itself.

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